Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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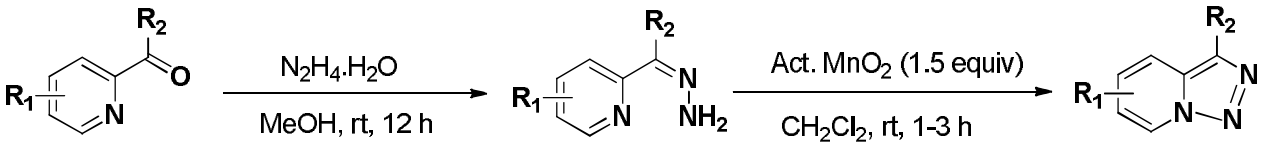
I. General Methods

All reagents were either commercially purchased or synthesized according to literature reports and were used as such for the reactions. ^{18}O cylinder was purchased from Aldrich. All reactions were conducted in over-dried glassware. Thin Layer Chromatography (TLC) was conducted using Merck silica gel 60 and flash column chromatography was performed using Merck silica gel 60. ^{1}H NMR was conducted on Bruker avance 300, Bruker avance 400 spectrometer and are reported in ppm as $SiMe_4$ as the reference relative to chloroform-d (δ= 7.26, singlet). Coupling data reported as: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, m = multiplet; coupling constant(s) in Hz. In addition, proton-decoupled ^{13}C NMR spectra were performed on Bruker avance 300 (75 MHz) and Bruker avance 400 (101 MHz) spectrometer and are reported in ppm using $CDCl_3$ as the internal standard. High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof mePermies Mass Spectroter. IR spectra were recorded as thin films on NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and were reported in frequency of absorption (cm^{-1}).

II. General procedure

i. Synthesis of [1,2,3]Triazolo[1,5-a]pyridine Substrates



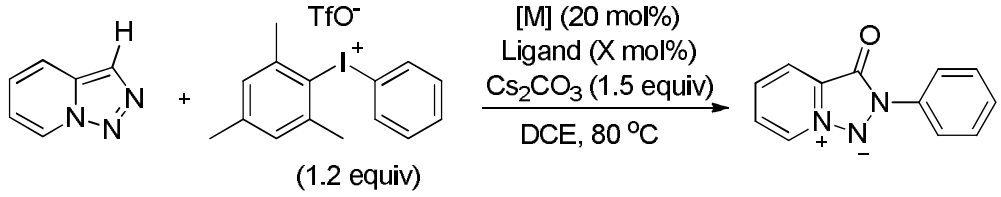
1 mmol (1 equiv) of pyridine carboxaldehyde/ketone was added to a solution of hydrazine monohydrate (3 mmol, 3.0 equiv) in 2 mL of methanol. The solution was stirred at rt for overnight before removing the solvent. Dichloromethane was added to the crude solid and the organic layer was extracted through aqueous work-up. The extract was dried using magnesium sulfate and the solvent was removed after filtration. The resulting hydrazone product was dissolved in 3 mL of dichloromethane and activated MnO_2 (approximately 1.5 equiv) was added in portions. The suspension was stirred at rt and the conversion was tracked using TLC. Upon

completion (1-3 h), the solid residue was filtered-out through celite and the triazolopyridine product was isolated through silica gel column chromatography.

ii. Copper-catalyzed aerobic carboxygenation and N-arylation of [1,2,3]Triazolo[1,5-a]pyridines: Optimization Studies

iia. Catalyst screening

To an oven-dried screw-cap vial (a schlenk tube was used for those reactions that were conducted under an oxygen atmosphere) was added the [1,2,3]triazolo[1,5-a]pyridine (0.1 mmol, 1 equiv), phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), metal catalyst (20% mmol), ligand (if any) and Cs_2CO_3 (0.2 mmol, 1.5 equiv). 1 mL of dry DCE was added and the reaction mixture was heated at 80 ^oC till consumption of the triazole completed (as per TLC). The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethylamine) column chromatography (hexane/ethyl acetate) to afford the desired product.



Entry	[M] (20 mol%)	Ligand/additive	Time (h)	Yield (%)
1	$Cu(OTf)_2$	_	12	No reaction
2	CuCN	_	12	15
3	CuI	_	12	34
4	CuBr	_	15	32
5	$Cu(OAc)_2$	_	12	No reaction
6	$CuBr_2$	_	12	28

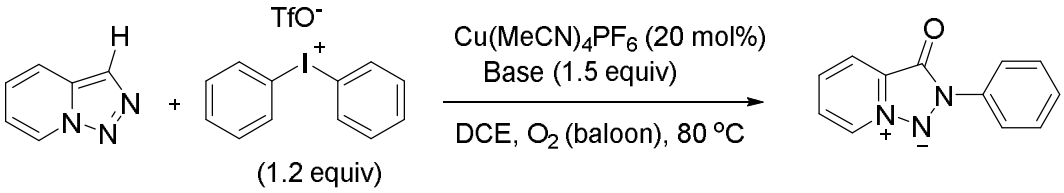
7	$CuCl_2$	_	12	24
7	$Cu(MeCN)_4PF_6$	_	12	41
8[a]	**$Cu(MeCN)_4PF_6$**	**_**	**4**	**62**
9[a] [b]	$Cu(MeCN)_4PF_6$	_	5	38
10[a] [c]	$Cu(MeCN)_4PF_6$	_	24	28
11[a] [d]	$Cu(MeCN)_4PF_6$	_	4	60
12[a]	$Cu(MeCN)_4PF_6$	1,10-phenanthroline (20 mol%)	6	37
13[a]	$Cu(MeCN)_4PF_6$	PPh_3 (40 mol%)	6	No reaction
14[a]	$Cu(MeCN)_4PF_6$	TMEDA (20 mol%)	6	15
15[a]	$Cu(MeCN)_4PF_6$	2,2'-bipyridyl (20 mol%)	8	20
16[a]	$Cu(MeCN)_4PF_6$	H_2O (50 mol%)	8	25
17[a]	$Cu(MeCN)_4PF_6$	H_2O_2 (2 equiv)	8	15
18[a]	$PdCl_2$	PPh_3(40 mol%)	12	No reaction
19[a]	AuCl	-	12	No reaction
20[a]	$FeCl_2$	-	12	No reaction
21[a]	-	-	12	No reaction

[a] Reaction carried-out under an oxygen balloon. [b] Reaction carried-out with 10 mol% of the catalyst. [c] Reaction carried-out at 50 °C. [d] Reaction carried-out at 90 °C. At 90 °C, formation of phenylacetamide which was derived from an aerobic oxidation reaction between the iodonium triflate and the acetonitrile ligand of the copper-catalyst was observed[1].

1. S-K Xiang, D-X. Zhang, H. Hu, J-L. Shi, L-G. Liao, C. Feng, B-Q. Wang, K-Q. Zhao, P. Hu, H. Yang, W-H. Yu, *Adv. Synth. Catal*. 2013, **355**, 1495

iib. Screening of the Base

To an oven-dried schlenk tube was added the [1,2,3]triazolo[1,5-a]pyridine (0.1 mmol, 1 equiv), phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), $Cu(MeCN)_4PF_6$ (20% mmol), and the base (0.15 mmol, 1.5 equiv). The tube was sealed and was evacuated and refilled with molecular oxygen (using an oxygen balloon, repeated three times). 1 mL of dry DCE was added and molecular oxygen was bubbled through the solution for a few seconds. The reaction mixture was then heated at 80 ^oC under an oxygen balloon till consumption of the triazole was observed through TLC. The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethyl amine) column chromatography (hexane/ethyl acetate) to afford the desired product.

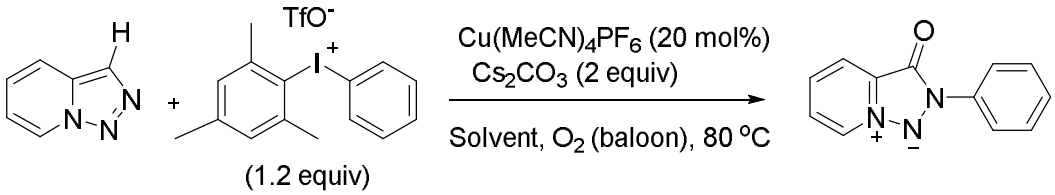


Entry	Base	Time (h)	Yield (%)
1	K_3PO_4	5	Decomposed
2	CsOAC	5	No reaction
3	K_2CO_3	5	Decomposed
5	2,6-di-tert-butylpyridine	5	Decomposed
6	NaOH	5	10
7	Na_2CO_3	5	30
8	Cs_2CO_3	4	65
9[a]	Cs_2CO_3	6	43
10[b]	**Cs_2CO_3**	**4**	**73**
10	-	2	Decomposed

[a] Reaction done with 1 equiv of the base. [b] Reaction done with 2 equiv of the base

iic. Screening of solvents

To an oven-dried schlenk tube was added the [1,2,3]triazolo[1,5-a]pyridine (0.1 mmol, 1 equiv), phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), $Cu(MeCN)_4PF_6$ (20% mmol), and Cs_2CO_3 (0.2 mmol, 2 equiv). The tube was sealed and was evacuated and refilled with molecular oxygen (using an oxygen balloon, repeated three times). 1 mL of dry solvent was added and molecular oxygen was bubbled through the solution for a few seconds. The reaction mixture was then heated at 80 ^oC under an oxygen balloon till consumption of the triazole was observed through TLC. The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethylamine) column chromatography (hexane/ethyl acetate) to afford the desired product.

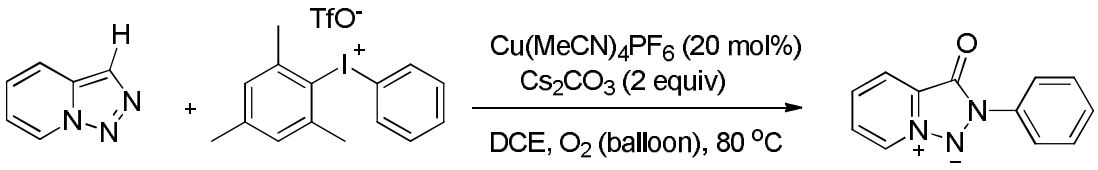


Entry	Solvent	Time (h)	Yield (%)
1	DMF	3	Decomposed
2	t-BuOH	3	Decomposed
3	Dioxane	24	No reaction
4	Toluene	12	20
5	DCE	4	70

iid. Screening of the stoichiometry for the triflate salt.

To an oven-dried schlenk tube was added the [1,2,3]triazolo[1,5-a]pyridine (0.1 mmol, 1 equiv), phenyl(mesityl)iodonium triflate (0.X mmol, X equiv), $Cu(MeCN)_4PF_6$ (20% mmol), and Cs_2CO_3 (0.2 mmol, 2 equiv). The tube was sealed and was evacuated and refilled with molecular oxygen (using an oxygen balloon, repeated three times). 1 mL of dry solvent was added and molecular oxygen was bubbled through the solution for a few seconds. The reaction mixture was

then heated at 80 °C under an oxygen balloon till consumption of the triazole was observed through TLC. The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethylamine) column chromatography (hexane/ethyl acetate) to afford the desired product.



Entry	Triflate salt (number of equiv)	Time (h)	Yield (%)
1	**1.2**	**4**	**73**
2	1.5	4	68
3	2.0	4	60
4	0	2	decomposition

iii. Optimized procedure for the catalysis reaction

To an oven-dried schlenk tube was added the triazolopyridine (0.1 mmol, 1 equiv), phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), $Cu(MeCN)_4PF_6$ (20% mmol), and the base (0.2 mmol, 2 equiv). The tube was sealed and was evacuated and refilled with molecular oxygen (using an oxygen balloon, repeated three times). 1 mL of dry DCE was added and molecular oxygen was bubbled through the solution for a few seconds. The reaction mixture was then heated at 80 °C under an oxygen balloon till consumption of the triazole was observed through TLC. The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethylamine) column chromatography (hexane/ethyl acetate) to afford the desired product.

iv. Procedure for the catalysis reaction under ^{18}O atmosphere.

To an oven-dried schlenk tube was added 13 mg of 7-methyl-[1,2,3]triazolo[1,5-a]pyridine **1b** (0.1 mmol, 1 equiv), 57 mg of phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), 7.5 mg

of $Cu(MeCN)_4PF_6$ (20% mmol), and 65 mg of Cs_2CO_3 (0.2 mmol, 2 equiv). The tube was sealed and was evacuated and refilled with ^{18}O (which was collected into a thick evacuated balloon from a 1-liter ^{18}O cylinder). 1 mL of dry DCE was added and the reaction mixture was then heated at 80 ^oC under the ^{18}O-balloon till the starting triazole consumed (4 h). The brown suspension was filtered through celite and the filtrate was concentrated by vacuum and purified through silica gel (basified with triethylamine) column chromatography (hexane/ethyl acetate) to afford the desired product **2b′** as an yellow solid (95%).

v. Procedure for the catalysis reaction in the presence of radical inhibitor BTC

To an oven-dried schlenk tube was added 13 mg of 7-methyl-[1,2,3]triazolo[1,5-a]pyridine **1b** (0.1 mmol, 1 equiv), 57 mg of phenyl(mesityl)iodonium triflate (0.12 mmol, 1.2 equiv), 7.5 mg of $Cu(MeCN)_4PF_6$ (20% mmol), 22 mg of 2,6-Di-tert-butyl-p-cresol (0.1 mmol, 1 equiv) and 65 mg of Cs_2CO_3 (0.2 mmol, 2 equiv). The tube was sealed and was evacuated and refilled with oxygen. 1 mL of dry DCE was added and the reaction mixture was then heated at 80 ^oC under the oxygen balloon. The TLC showed total decomposition within 1 h.

vi. Procedure for the palladium-catalyzed C7-arylation of 2a

To an oven-dried schlenk tube was added 26 mg (0.125 mmol, 1 equiv) of **2a**, 3 mg (10 mol%) of $Pd(OAc)_2$, 6.5 mg (20 mol%) of PPh_3, 122 mg (0.38 mmol, 3 equiv) of Cs_2CO_3. 1 mL of dry toluene was added followed by 0.028 mL (0.25 mmol, 2 equiv) of phenyl iodide. The suspension was heated at 100 ^oC till the starting material was consumed (48 h). The reaction mixture was filtered over celite and the product was purified through silica gel column chromatography (Hexane/Ethyl acetate) to obtain 21 mg (58%) of the arylated product **3a** as an yellow solid.

vii. Procedure for the catalytic hydrogenation of 2b

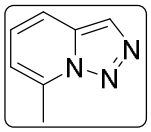
To an oven-dried schlenk tube was added 21 mg (0.1 mmol, 1 equiv) of **2b**. The tube was evacuated and backfilled with nitrogen. 1 mL of methanol was added followed by a pinch of platinum on carbon. The reaction mixture was stirred at room temperature in the presence of a hydrogen balloon. The yellow color of the initial solution changed to colorless in 3 h and TLC showed the complete consumption of the starting material. Filtered over celite and the solvent

was removed under vacuum to obtain 22 mg of the partially hydrogenated product **4** as a white solid. No further purification was necessary.

III. Analytical data

i. Analytical data for the Triazolopyridine substrates

1. 7-methyl-[1,2,3]triazolo[1,5-a]pyridine (**1b**):



Pale yellow solid (76% overall isolated yield).

R_f = 0.38 (1:1 Hexane:Ethyl acetate); M.P: 52-54 ^oC

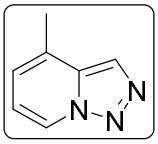
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.79 (s, 3H), 6.70 (d, *J* = 9.2 Hz, 1H), 7.10-7.13 (m, 1H), 7.54 (d, *J* = 12 Hz, 1H), 8.01 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 17.03, 113.91, 115.01, 125.01, 125.60, 133.61, 135.25

IR (film) / cm^{-1}: 3053, 2986, 2305, 1422, 1265, 895, 738, 704

HRMS (ESI): Calculated for $C_7H_7N_3$ m/z 134.0719, found 134.0722.

2. 4-methyl-[1,2,3]triazolo[1,5-a]pyridine (**1c**)



Pale white solid (78% overall yield)

R_f = 0.36 (1:1 Hexane:Ethyl acetate); M.P: 54-57 ^oC

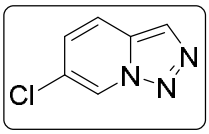
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.51 (s, 3H), 6.92-6.83 (m, 1H), 7.00-6.93 (m, 1H), 8.04-7.98 (m, 1H), 8.61-8.53 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 18.24, 115.44, 122.90, 123.97, 124.88, 128.69, 135.11

IR(film) / cm^{-1}: 3053, 2981, 2305, 1421, 1255, 895, 738, 704

HRMS (ESI): Calculated for $C_7H_7N_3$ m/z: 134.0719; found: 133.0722

3. 6-chloro-[1,2,3]triazolo[1,5-a]pyridine (**1d**)



Pale yellow solid (66% overall yield)

R_f = 0.43 (1:1 Hexane:Ethyl acetate); M.P: 94-96 ^oC

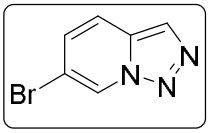
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.16 (d, *J* = 9.4 Hz, 1H), 7.65 (d, *J* = 9.45 Hz, 1H), 8.00 (s, 1H), 8.71 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.14, 123.18, 123.96, 126.17, 127.01, 132.15

IR (film) / cm^{-1}: 3053, 2985, 2304, 1506, 1421, 1255, 738, 704

HRMS (ESI): calculated for $C_6H_4ClN_3$ m/z 154.0173; found: 154.0176

4. 6-bromo-[1,2,3]triazolo[1,5-a]pyridine (**1e**)



Pale white solid (72% overall yield)

R_f = 0.41 (1:1 Hexane:Ethyl acetate); M.P: 88-90 ^oC

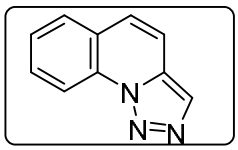
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.35-7.28 (m, 1H), 7.63 (d, *J* = 9.30 Hz, 1H), 8.06 (s, 1H), 8.90 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 110.78, 118.40, 125.63, 126.38, 129.18, 132.40

IR (film) / cm^{-1}: 3053, 2985, 2304, 1506, 1421, 1255, 738, 704

HRMS (ESI): calculated for $C_6H_4BrN_3$ m/z 197.9668; found: 197.9668

5. [1,2,3]triazolo[1,5-a]quinolone (**1f**)



Pale yellow solid (65% overall yield)

R_f = 0.38 (1:1 Hexane:Ethyl acetate); M.P: 110-114 ^oC

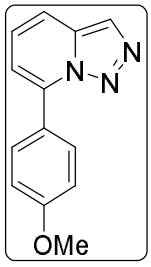
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54-7.46 (m, 3H), 7.60-7.53 (m, 1H), 7.75-7.69 (m, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 8.09 (s, 1H), 8.75 (d, *J* = 8.4 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 114.85, 116.43, 123.99, 126.80, 127.22, 127.65, 128.64, 130.17, 131.86, 131.96

IR (film) / cm^{-1}: 3053, 2985, 2304, 1662, 1421, 1255, 738, 704

HRMS (ESI): calculated for $C_{10}H_7N_3$ m/z 170.0719; found: 170.0716

6. 7-(4-methoxyphenyl)-[1,2,3]triazolo[1,5-a]pyridine (**1g**)



Pale yellow solid (78% overall yield)

R_f = 0.51 (Hexane/Ethyl acetate, 1:1); M.P: 103-105 ^oC

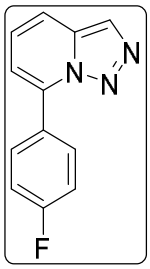
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.89 (s, 3H), 7.00-7.02 (m, 1H), 7.06-7.08 (m, 2H), 7.30-7.33 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.97-8.00 (m, 2H), 8.14 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 55.44, 114.08, 114.27, 115.85, 124.45, 125.56, 125.88, 128.14, 130.68, 134.79, 138.39, 161.01

IR (film) / cm^{-1}: 3053, 2986, 2305, 1422, 1265, 895, 748, 704

HRMS (ESI) calculated for $C_{13}H_{11}N_3O$ m/z 226.0981, found 226.0981.

7. 7-(4-fluorophenyl)-[1,2,3]triazolo[1,5-a]pyridine (**1h**):



Pale yellow solid (78% overall isolated yield).

R_f: 0.43 (Hexane/Ethyl acetate, 1:1); M.P: 134-135 ºC

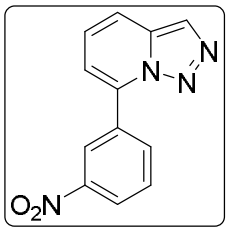
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 7.02 (dd, *J* = 6.9 Hz, 1.1 Hz, 1H), 7.19-7.28 (m, 2H), 7.31-7.37 (m, 1H), 7.74 (dd, *J* = 8.9 Hz, 1.0 Hz, 1H), 7.99-8.04 (m, 2H), 8.16 (s, 1H)

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 115.01, 115.59, 115.88, 116.69, 125.53, 126.09, 128.13, 128.17, 131.21, 131.32,134.71, 137.41, 161.96, 165.28

IR (film) / cm^{-1}: 3053, 2986, 2304, 1422, 1265, 895, 748, 704

HRMS (ESI) calculated for $C_{12}H_8FN_3$ m/z 214.0781, found 214.0786.

8. 7-(3-nitrophenyl)-[1,2,3]triazolo[1,5-a]pyridine (**1i**)



yellow solid (62% overall isolated yield).

R_f: 0.39 (Hexane/Ethyl acetate, 1:1); M.P: 196-199 ºC

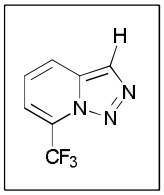
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17 (d, *J* = 6.8 Hz, 1H), 7.38-7.42 (m, 1H), 7.76 (t, *J* = 8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 8.21 (s, 1H), 8.38 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.83 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 115.90, 118.03, 124.22, 124.75, 125.42, 126.48, 129.73, 133.59, 134.70, 135.14, 135.88, 148.49

IR (film) / cm^{-1}: 3053, 2986, 2305, 1422, 1265, 895, 741, 706

HRMS (ESI) calculated for $C_{12}H_8N_4O_2$ m/z 241.0726, found 241.0730.

9. 7-(trifluoromethyl)-[1,2,3]triazolo[1,5-a]pyridine



Pale yellow solid (70% overall isolated yield).

R_f: 0.45 (Hexane/Ethyl acetate, 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 7.39-7.31 (m, 1H), 7.46-7.40 (m, 1H), 7.97 (d, *J* = 9.20Hz, 1H), 9.23 (s, 1H)

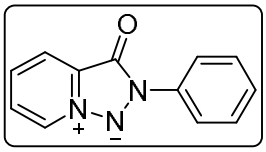
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 115.17, 115.21, 115.26, 118.66, 121.37, 121.92, 123.87, 126.63, 134.45

IR (film) / cm^{-1}: 3056, 2956, 2288, 1655, 1422, 1245, 856, 726, 704

HRMS (ESI) calculated for $C_7H_4F_3N_3$ m/z 188.0436, found 188.0438

ii. Analytical data for pyridinium triazolinone ylides

1. 3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridine-8-ium-1-ide (**2a**)



yellow solid

R_f: 0.27 (Hexane/Ethyl acetate, 1:1), M.P: 175-177 ^oC

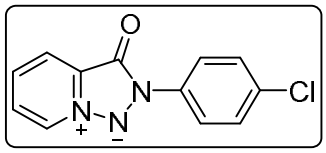
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.86-6.90 (m, 1H), 7.10 (td, *J* = 6.9 Hz, 1.4 Hz, 1H), 7.32-7.36 (m, 1H), 7.46-7.50 (m, 2H), 7.82 (dd, *J* = 8.68 Hz, 1.1 Hz, 1H), 8.11-8.16 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.46, 121.09, 122.16, 122.31, 122.48, 122.97, 127.42, 129.15, 136.36, 152.51

IR (film) / cm^{-1}: 3053, 2986, 2305, 1647, 1422, 1265, 1142, 895, 748, 704

HRMS (ESI) calculated for $C_{12}H_9N_3O$ m/z 212.0825, found 212.0826.

2. 2-(4-chlorophenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridine-8-ium-1-ide (**2b**)



Yellow solid

R_f: 0.09 (Hexane/Ethyl acetate, 1:1), M.P: 142-145 ^oC

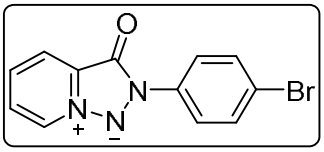
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.91-6.94 (m, 1H), 7.14-7.18 (m, 1H), 7.46 (d, *J* =7.8 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 1H), 8.12-8.18 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.77, 122.01, 122.22, 122.56, 122.98, 129.29, 132.88, 134.94, 152.49

IR (film) / cm^{-1}: 3053, 2986, 2305, 1647, 1422, 1325, 1265, 895, 746, 706

HRMS (ESI) calculated for $C_{12}H_8ClN_3O$ m/z 246.0435, found 246.0438.

3. 2-(4-bromophenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridine-8-ium-1-ide (**2c**)



yellow solid

R_f: 0.09 (Hexane/Ethyl acetate, 1:1), M.P: 174-175 ^oC

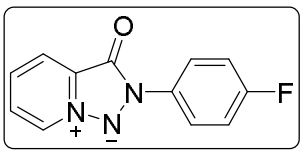
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.92-6.96 (m, 1H), 7.17, (td, *J* = 7.0 Hz, 1.4 Hz, 1H), 7.60-7.64 (m, 2H), 7.85 (dt, *J* = 8.7 Hz, 1.1 Hz, 1H), 8.11-8.13 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.74, 120.82, 122.25, 122.58, 122.97, 123.16, 132.26, 135.49, 152.50

IR (film) / cm^{-1}: 3422, 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 746, 704

HRMS (ESI) calculated for $C_{12}H_8BrN_3O$ m/z 289.9930, found 289.9934.

4. 2-(4-fluorophenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2d**)



yellow solid

R_f: 0.09 (Hexane/Ethyl acetate, 1:1), M.P: 178-180 ^oC

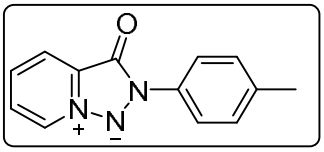
^1H NMR (400 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 6.91-6.95 (m, 1H), 7.13-7.21 (m, 3H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.13-8.18 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 115.91, 116.13, 118.64, 122.22, 122.37, 122.48, 122.91, 122.96, 122.99, 132.50, 132.53, 152.38, 160.25, 162.71

IR (film) / cm^{-1}: 3050, 2998, 2305, 1625 1422, 1325, 1345, 1265, 1142, 746, 704

HRMS (ESI) calculated for $C_{12}H_8FN_3O$ m/z 230.0730, found 230.0730.

5. 3-oxo-2-(p-tolyl)-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridine-8-ium-1-ide (**2f**)



yellow solid

R_f: 0.10 (Hexane/Ethyl acetate, 1:1), M.P: 160-164 ^oC

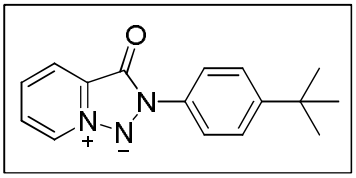
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.40 (s, 3H), 6.88-6.92 (m, 1H), 7.13 (td, *J* = 6.9 Hz, 1.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 7 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 21.14, 118.30, 121.11, 122.09, 122.18, 122.44, 122.93, 129.70, 133.92, 137.41, 152.41

IR (film) / cm^{-1}: 3429, 3422, 3412, 3053, 2986, 2305, 1647, 1510, 1422, 1325, 1265, 1142, 895, 741, 704, 507

HRMS (ESI) calculated for $C_{13}H_{11}N_3O$ m/z 226.0981, found 226.0986.

6. 2-(6-(tert-butyl)pyridin-3-yl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2g**)



yellow solid

R_f: 0.13 (Hexane/Ethyl acetate, 1:1), M.P: 200-203 ^oC

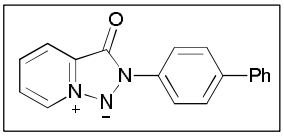
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.36 (s, 9H), 6.92-8.87 (m, 1H), 7.12 (dt, *J* = 7.0, 1.5Hz, 1H), 7.52 (d, *J* = 8.6Hz, 2H), 7.85 (d, *J* = 8.7Hz, 1H), 8.06-8.01 (m, 2H), 8.13 (d, *J* = 7.6Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 31.30, 34.71, 118.3, 121.0, 122.0, 122.1, 122.3, 122.9, 126.0, 133.7, 150.6, 152.4

IR (film) / cm^{-1}: 3053, 2966, 2348, 1658, 1514, 1371, 1319, 1270, 1141, 728, 704

HRMS (ESI) calculated for $C_{16}H_{17}N_3O$ m/z 268.1451, found 268.1448

7. 2-([1,1'-biphenyl]-4-yl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2h**)



yellow solid

R_f: 0.12 (Hexane/Ethyl acetate, 1:1), M.P: 154-157 ºC

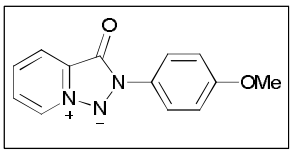
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):6.92 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.40-7.34 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.66-7.61 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 1H), 8.16 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 8.6 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.69, 121.45, 122.40, 122.50, 122.69, 123.16, 127.25, 127.76, 127.97, 129.04, 135.70, 140.39, 152.74

IR (film) / cm^{-1}: 3053, 2985, 1658, 1421, 1280, 894, 720, 695

HRMS (ESI) calculated for $C_{18}H_{13}N_3O$ m/z 288.1138, found 288.1134

8. 2-(4-methoxyphenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2i**)



yellow solid

R_f: 0.14 (Hexane/Ethyl acetate, 1:1), M.P: 174-177 ^oC

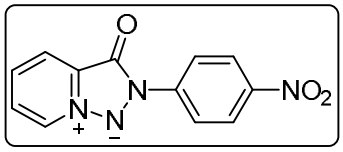
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.86 (s, 3H), 6.94-6.88 (m, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.12 (t, *J* = 7.0 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 8.13 (d, *J* = 7.4 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 55.73, 114.53, 118.61, 121.97, 122.15, 122.30, 123.10, 129.66, 159.01

IR (film) / cm^{-1}: 3025, 2985, 1670, 1410, 1265, 984, 725, 705

HRMS (ESI) calculated for $C_{13}H_{11}N_3O_2$ m/z 242.0930, found 242.088

9. 2-(4-nitrophenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2j**)



yellow solid

R_f: 0.08 (Hexane/Ethyl acetate, 1:1), M.P: 223-225 ^oC

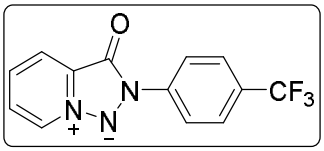
^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.97-7.01 (m, 1H), 7.23-7.26 (m, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 8.37 (d, *J* = 9.2 Hz, 2H), 8.53 (d, *J* = 9.2 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 119.29, 120.26, 122.50, 123.03, 123.46, 123.66, 124.87, 141.30, 145.80, 153.14

IR (film) / cm^{-1}: 3422, 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 743, 706

HRMS (ESI) calculated for $C_{12}H_8N_4O_3$ m/z 257.0675, found 257.0675.

10.3-oxo-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2k**)



yellow solid

R_f: 0.13 (Hexane/Ethyl acetate, 1:1), M.P. 195-198 ^oC

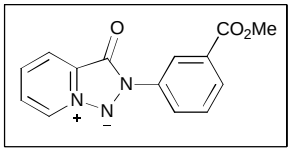
^1H NMR (400 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 6.94-6.97 (m, 1H), 7.20 (td, *J* = 7.0 Hz, 1.4 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 8.40 (d, *J* = 8.5 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm, ^{19}F-coupled): 118.87, 120.46, 122.35, 122.54, 122.69, 122.93, 122.99, 125.24, 126.29, 126.33, 126.37, 126.40, 128.81, 129.13, 139.18, 152.85

IR (film) / cm^{-1}: 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 750, 704

HRMS (ESI) calculated for $C_{13}H_8F_3N_3O$ m/z 280.0698, found 280.0692.

11. 2-(3-(methoxycarbonyl)phenyl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2m**)



yellow solid

R_f: 0.12 (Hexane/Ethyl acetate, 1:1), M.P: 200-203 ^oC

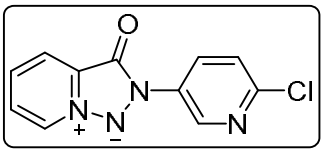
1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.77-8.72 (m, 1H), 8.54-8.49 (m, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.17 (dt, *J* = 7.1, 1.5 Hz, 1H), 6.96-6.90 (m, 1H), 3.95 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 52.36, 118.74, 121.82, 122.21, 122.55, 122.62, 123.02, 125.13, 128.32, 129.33, 131.37, 136.57, 152.63, 166.34

IR (film) / cm^{-1}: 3053, 2985, 2409, 1722, 1666, 1421, 1230, 894, 723, 704

HRMS (ESI) calculated for $C_{14}H_{11}N_3O_3$ m/z 270.0879, found 270.0880

12.2-(6-chloropyridin-3-yl)-3-oxo-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2n**)



brown solid

R_f: 0.09 (Hexane/Ethyl acetate, 1:1), M.P: 154-156 °C

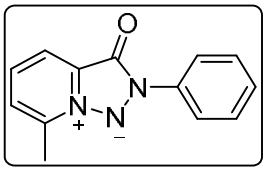
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.97-7.00 (m, 1H), 7.22 (td, *J* = 7.0 Hz, 1.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.86-7.88 (m, 1H), 8.18 (d, *J* = 7.1 Hz, 1H), 8.70 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 9.20 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 119.22, 122.29, 123.07, 124.38, 130.20, 132.37, 141.48, 149.18, 152.94

IR (film) / cm^{-1}: 3422, 3420, 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 748, 704, 503

HRMS (ESI) calculated for $C_{11}H_7ClN_4O$ m/z 247.0387, found 247.0387.

13. 7-methyl-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2o**)



yellow solid

R_f: 0.13 (Hexane/Ethyl acetate, 1:1), M.P: 166-168 °C

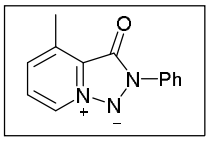
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.64 (s, 3H), 6.89-6.94 (m, 1H), 7.01 (d, *J* = 6.9 Hz, 1H), 7.33-7.37 (m, 1H), 7.48-7.53 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 8.21-8.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 16.17, 118.79, 119.60, 121.12, 121.19, 122.81, 127.29, 129.11, 132.92, 136.66, 153.02

IR (film) / cm^{-1}: 3053, 2986, 2305, 1647, 1422, 1265, 1142, 895, 741, 706

HRMS (ESI) calculated for $C_{13}H_{11}N_3O$ m/z 226.0981, found 226.0985.

14. 4-methyl-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2p**)



yellow solid

R_f: 0.14 (Hexane/Ethyl acetate, 1:1), M.P: 158-161 ^{o}C

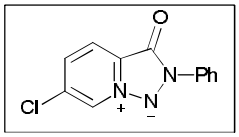
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.75 (s, 3H), 6.60 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 7.37-7.32 (m, 1H), 7.52-7.46 (m, 2H), 7.98 (d, *J* = 7.4 Hz, 1H), 8.16 (dd, *J* = 8.8, 1.3 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 16.52, 118.74, 120.80, 121.14, 121.65, 122.21, 127.42, 129.26, 136.51, 135.60, 153.41

IR (film) / cm^{-1}: 3180, 3155, 1654, 1494, 1313, 1285, 1130, 710, 704

HRMS (ESI) calculated for $C_{13}H_{11}N_3O$ m/z 226.0981, found 226.0981

15. 6-chloro-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2q**)



yellow solid

R_f: 0.16 (Hexane/Ethyl acetate, 1:1), M.P: 145-148 ^{o}C

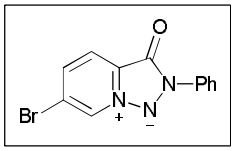
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.86 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.40-7.33 (m, 1H), 7.54-7.46 (m, 2H), 7.79 (d, *J* = 9.3 Hz, 1H), 8.12 (d, *J* = 8.9 Hz, 2H), 8.18 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 120.16, 121.11, 121.15, 121.18, 122.61, 127.82, 129.39, 131.62, 136.26, 152.46

IR (film) / cm^{-1}: 3145, 3098, 2310, 1668, 1421, 1234, 894, 789, 752

HRMS (ESI) calculated for $C_{12}H_8ClN_3O$ m/z 246.0435, found 246.0429

16. 6-bromo-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2r**)



yellow solid

R_f: 0.17 (Hexane/Ethyl acetate, 1:1), M.P: 141-145 °C

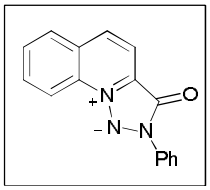
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.97 (dd, *J* = 9.2, 1.6 Hz, 1Hz), 7.40-7.39 (m, 1H), 7.54-7.46 (m, 2H), 7.72 (d, *J* = 9.4 Hz, 1H), 8.12 (dd, *J* = 8.9, 1.3 Hz, 2H), 8.30 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 118.78, 119.98, 121.22, 122.31, 122.63, 123.19, 124.38, 127.85, 129.14, 129.40, 136.22, 152.52

IR (film) / cm^{-1}: 3112, 3075, 2388, 1650, 1480, 1320, 1246, 910, 770, 715

HRMS (ESI) calculated for $C_{12}H_8BrN_3O$ m/z 289.9930, found 289.9932

17. 3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]quinolin-10-ium-1-ide (**2s**)



yellow solid

R_f: 0.13 (Hexane/Ethyl acetate, 1:1), M.P: 150-155 °C

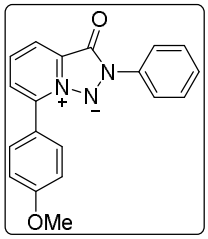
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.22 (m, 1H), 7.44-7.39 (m, 1H), 7.59-7.52 (m, 2H), 7.74-7.63 (m, 3H), 7.84-7.78 (m, 1H), 8.27 (d, *J* = 8.9 Hz, 2H), 8.53 (d, *J* = 8.9 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 116.08, 117.36, 118.97, 119.91, 121.50, 127.80, 127.99, 128.92, 129.20, 129.36, 129.44, 130.54, 136.69, 153.58

IR (film) / cm^{-1}: 3834, 3695, 3053, 2304, 2985, 1660, 1230, 894, 780, 705

HRMS (ESI) calculated for $C_{16}H_{11}N_3O$ m/z 262.0981, found 262.0986

18. 7-(4-methoxyphenyl)-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2t**)



yellow solid

R_f: 0.15 (Hexane/Ethyl acetate, 1:1), M.P: 172-174 ºC

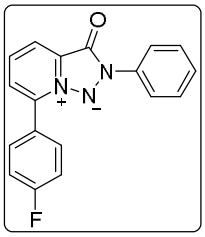
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.91 (s, 3H), 7.01-7.08 (m, 3H), 7.20 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.32-7.36 (m, 1H), 7.46-7.50 (m, 2H), 7.85(dd, *J* = 8.6, 1.2 Hz, 1H), 7.89-7.91 (m, 2H), 8.18 (d, *J* = 7.6 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 55.43, 114.12, 119.26, 120.23, 121.14, 121.78, 123.19, 123.67, 127.28, 129.07, 130.25, 135.07, 136.59, 152.77, 161.00

IR (film) / cm^{-1}: 3422, 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 748, 704

HRMS (ESI) calculated for $C_{19}H_{15}N_3O_2$ m/z 318.1243, found 318.1240.

19.7-(4-fluorophenyl)-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2u**)



yellow solid

R_f: 0.11 (Hexane/Ethyl acetate, 1:1), M.P: 156-159 ^oC

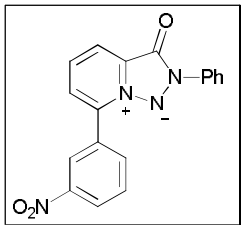
^1H NMR (400 MHz, $CDCl_3$) δ (ppm, ^{19}F coupled): 7.03-7.06 (m, 1H), 7.20-7.27 (m, 3H), 7.33-7.36 (m, 1H), 7.47-7.51 (m, 2H), 7.90-7.95 (m, 3H), 8.15-8.17 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm, ^{19}F coupled): 115.82, 116.04, 119.17, 121.04, 121.11, 122.47, 123.69, 126.97, 127.00, 127.43, 129.14, 130.85, 130.93, 134.19, 136.46, 152.74, 162.36, 164.86

IR (film) / cm^{-1}: 3447, 3429, 3422, 3412, 3053, 2986, 2305, 1647, 1422, 1325, 1265, 1142, 895, 743, 706

HRMS (ESI) calculated for $C_{18}H_{12}FN_3O$ m/z 306.1043, found 306.1040.

20. 7-(3-nitrophenyl)-3-oxo-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2v**)



Yellow-brown solid

R_f: 0.12 (Hexane/Ethyl acetate, 1:1), M.P: 198-202 ^oC

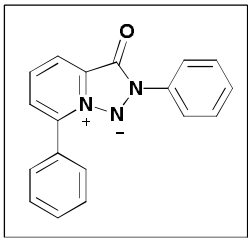
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13-7.06 (m, 1H), 7.39-7.32 (m, 2H), 7.50 (t, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.97 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.3 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.90-8.87 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 119.05, 121.03, 122.32, 123.33, 123.83, 123.90, 124.85, 127.62, 129.23, 129.87, 132.40, 134.42, 136.23, 148.47, 152.60

IR (film) / cm^{-1}: 3112, 2924, 2310, 1685, 1411, 1255, 918, 728, 705

HRMS (ESI) calculated for $C_{18}H_{12}N_4O_3$ m/z 333.0988, found 333.0988

21. 3-oxo-2,7-diphenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**3a**)



yellow solid

R_f: 0.11 (Hexane/Ethyl acetate, 1:1); M.P: 140-143 ^{o}C

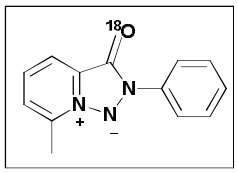
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09-7.03 (m, 1H), 7.27-7.24 (m, 1H), 7.38-7.33 (m, 1H), 7.50 (t, *J* = 8.2 Hz, 2H), 7.61-7.54 (m, 3H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.97-7.93 (m, 2H), 8.19 (d, *J* = 8.8 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 119.19, 121.12, 122.55, 127.33, 128.70, 128.75, 129.07, 130.22, 130.91, 132.03, 132.16, 135.15, 136.50, 152.73

IR (film) / cm^{-1}: 3053, 2985, 2388, 1658, 1436, 1421, 1288, 1178, 1120, 894, 770, 710

HRMS (ESI) calculated for $C_{18}H_{13}N_3O$ m/z 288.1138, found 288.1142

22. 7-methyl-3-(oxo-18O)-2-phenyl-2,3-dihydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**2i′**)



yellow solid

R_f: 0.13 (Hexane/Ethyl acetate, 1:1), M.P: 166-168 ºC

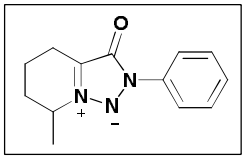
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.63 (s, 3H), 6.94-6.89 (m, 1H), 7.02-6.98 (m, 1H), 7.37-7.36-7.35 (m, 1H), 7.51 (t, *J* = 7.88 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 16.34, 118.98, 119.79, 121.29, 121.35, 122.94, 127.45, 129.27, 133.08, 136.78, 153.13

IR (film) / cm^{-1}: 3043, 2981, 2305, 1689, 1426, 1265, 1134, 898, 741, 706

HRMS (ESI) calculated for $C_{13}H_{11}N_3{}^{18}O$ m/z 228.1024, found 228.1024

23. 7-methyl-3-oxo-2-phenyl-2,3,4,5,6,7-hexahydro-[1,2,3]triazolo[1,5-a]pyridin-8-ium-1-ide (**4**)



Pale white solid

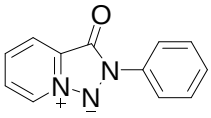
R_f: 0.21 (Hexane/Ethyl acetate, 1:1), M.P: 103-104 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.68 (d, *J* = 6.8 Hz, 3H), 1.89-1.78 (m, 2H), 2.11-2.00 (m, 1H), 2.31-2.16 (m, 1H), 2.76-2.63 (m, 1H), 2.90-2.79 (m, 1H), 4.43-4.31 (m, 1H), 7.37-7.30 (m, 1H), 7.47 (t, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H)

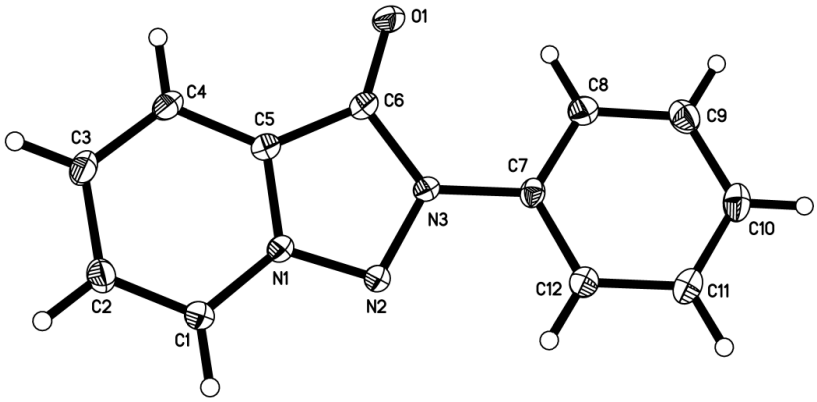
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 18.03, 19.99, 20.17, 30.71, 55.53, 116.56, 121.13, 127.41, 129.13, 136.74, 155.75

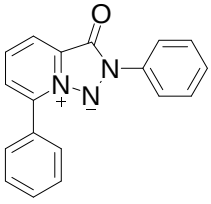
HRMS (ESI) calculated for $C_{13}H_{15}N_3O$ m/z 230.1294, found 230.1296

iii. X-ray crystal structures of 2a and 3a

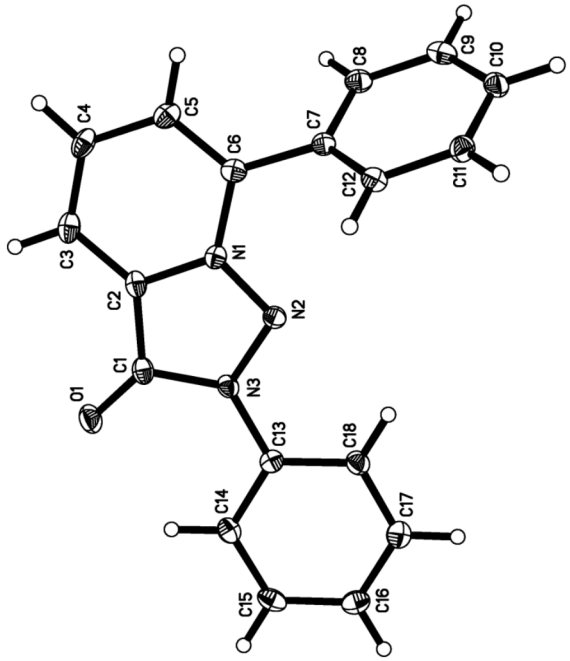


2a

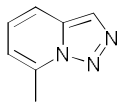


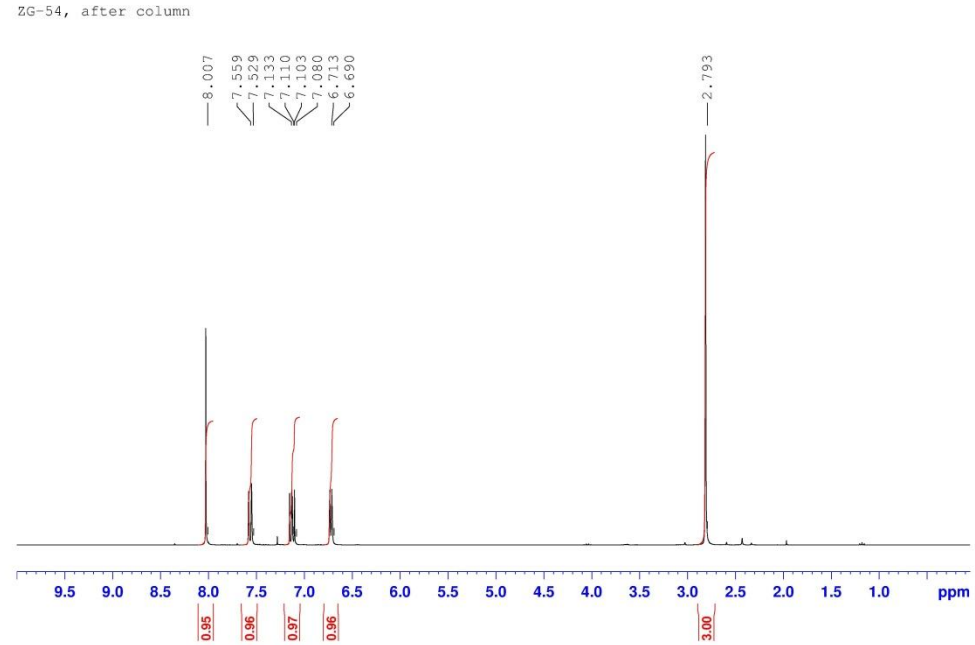


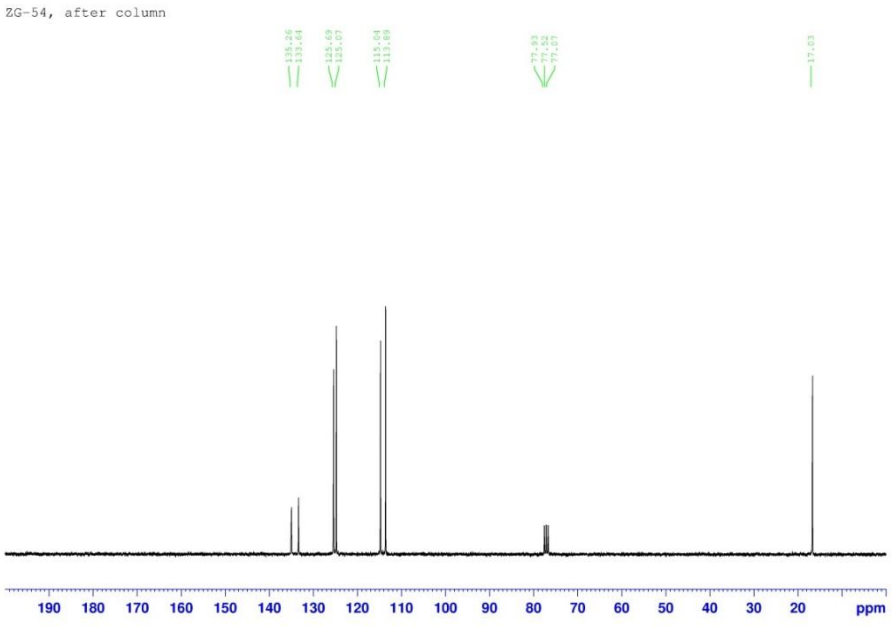
3a

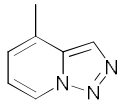


IV. Spectral images

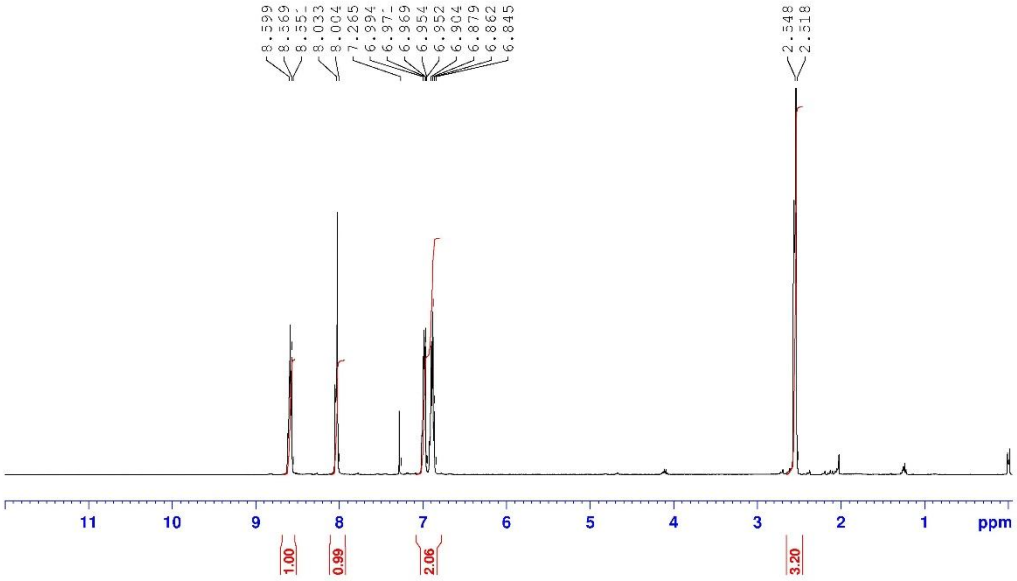
1. 



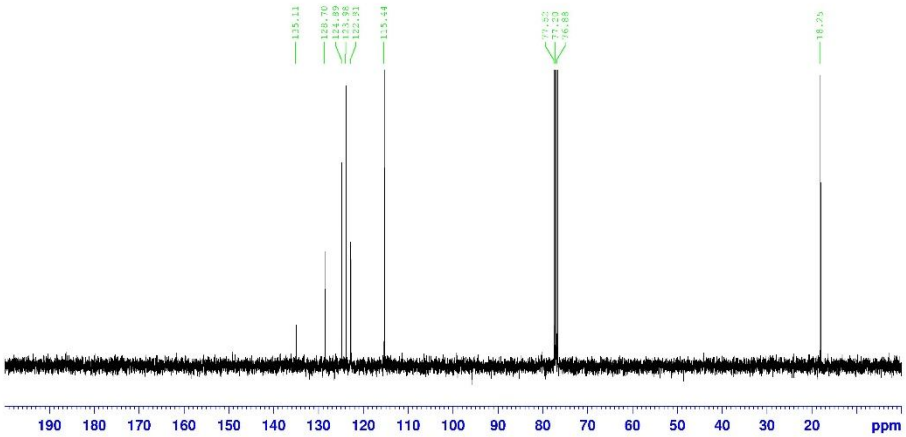


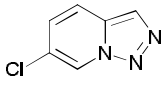
2. 

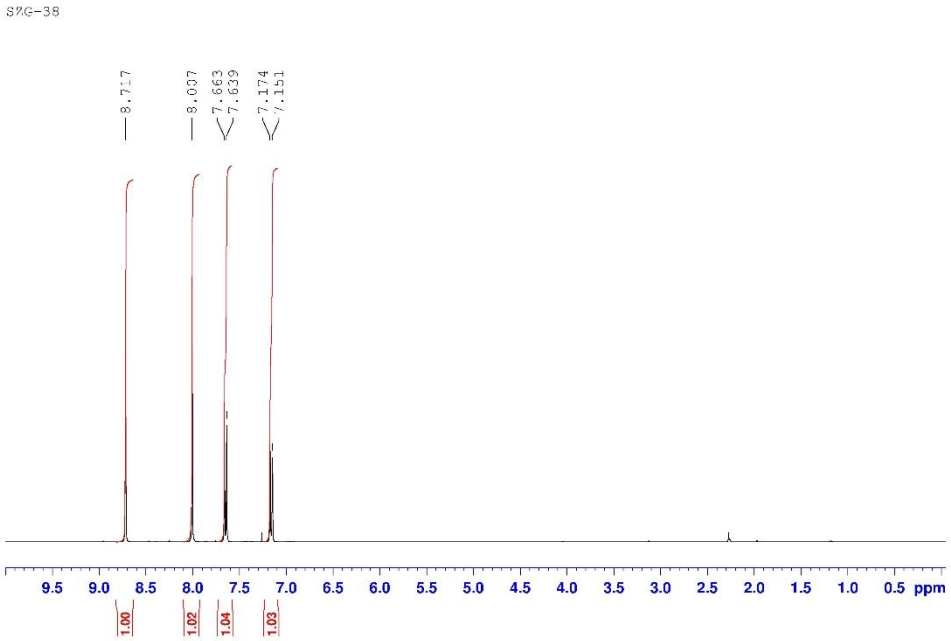
SZG70b, methyl substituted triazole

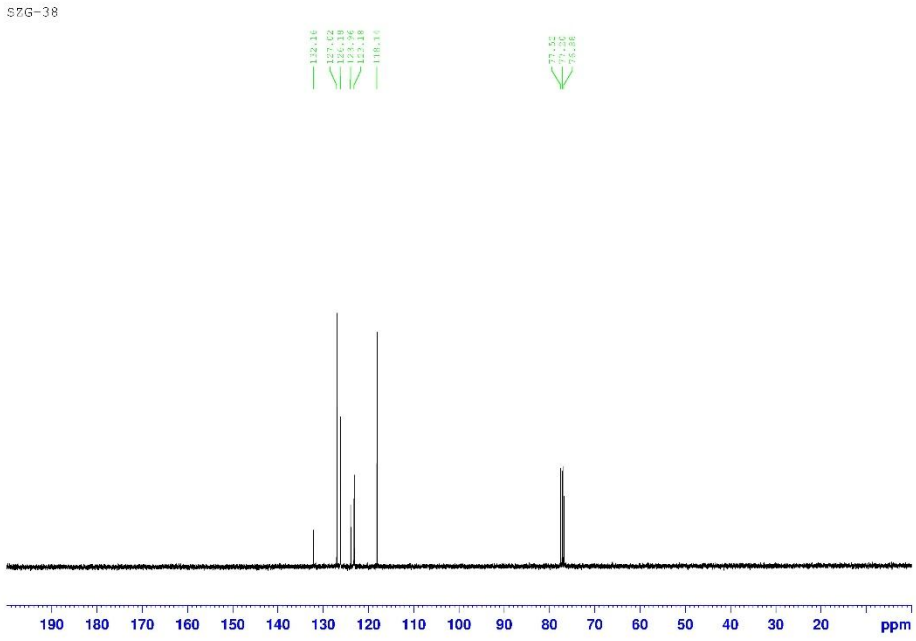


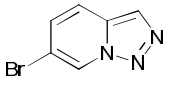
SZG-70B, methyl substituted triazole



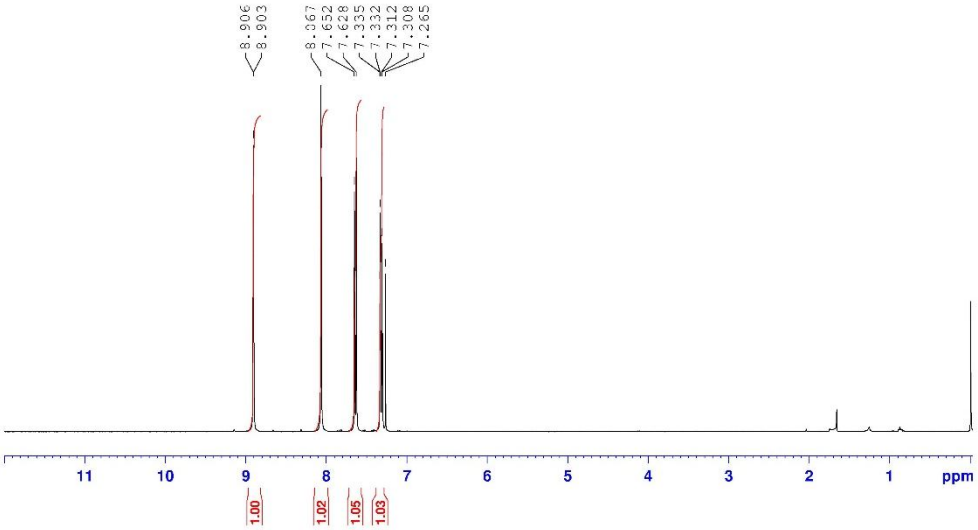
3. 
Cl
N
N
N


SZG-38
8.717
8.007
7.663
7.639
7.174
7.151
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.02
1.04
1.03

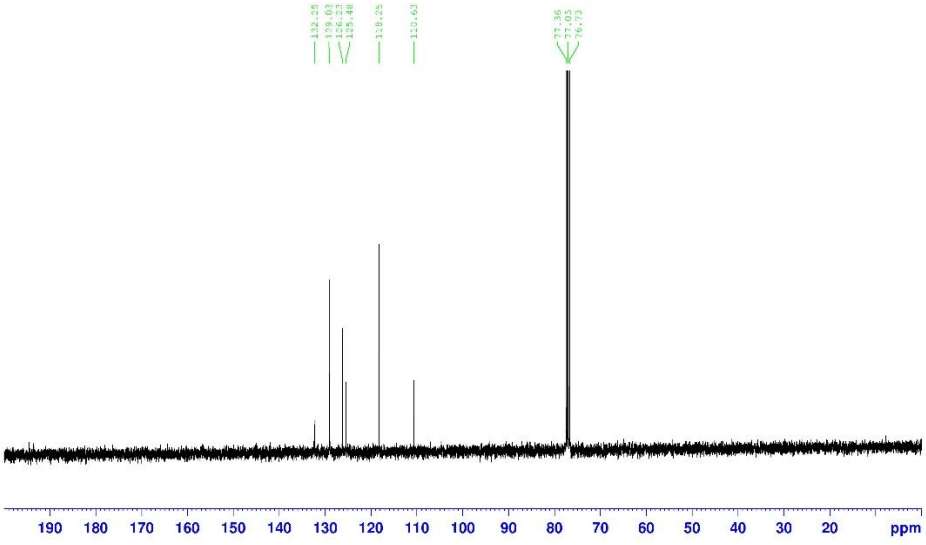

SZG-38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

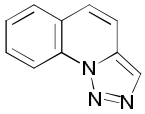
4. 

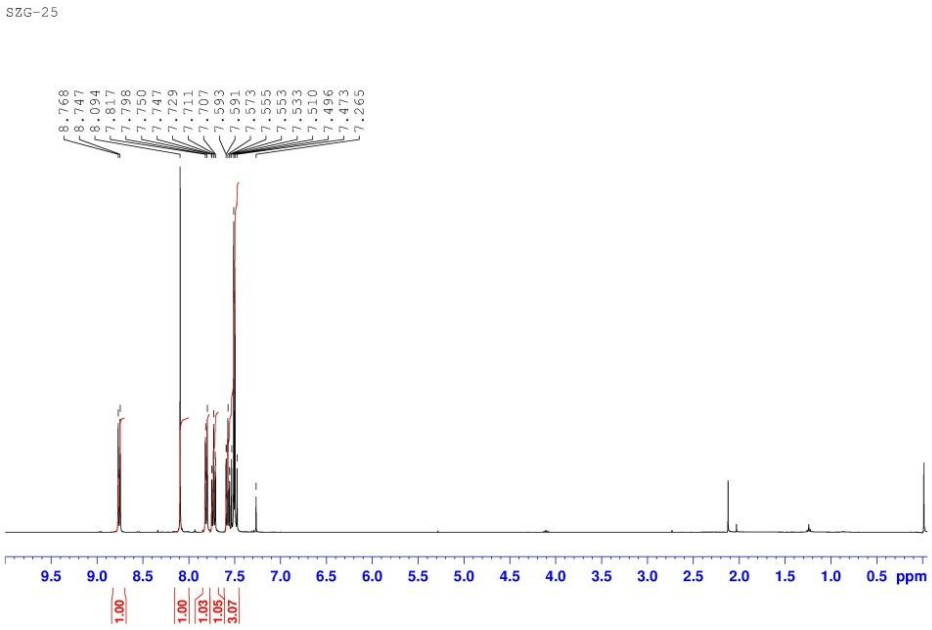
SZG70c, Br substituted triazole

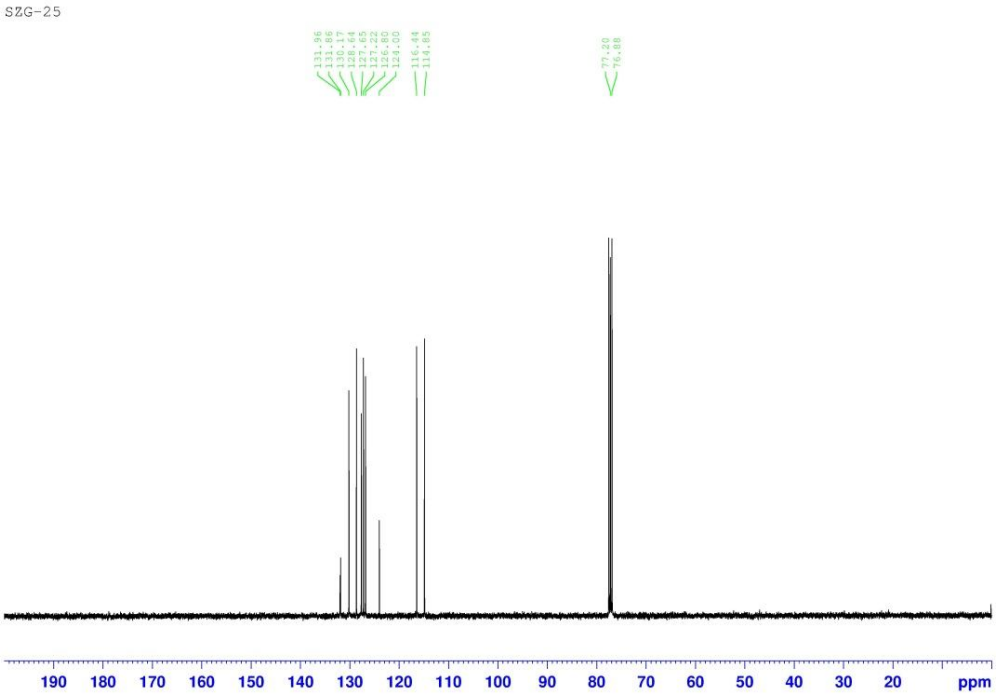


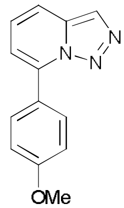
SZG-70C, Br substituted triazole

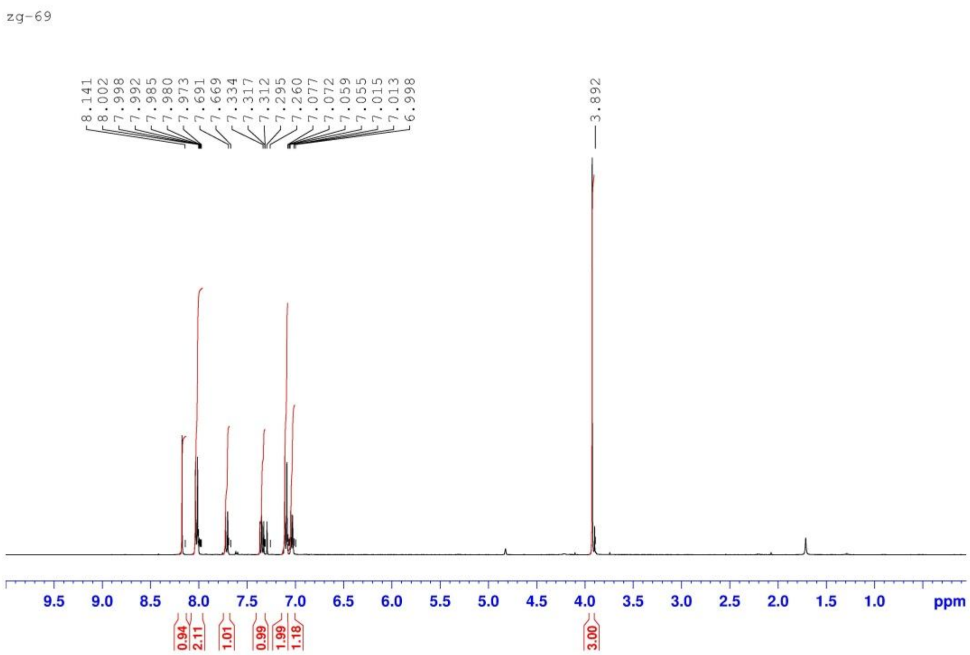


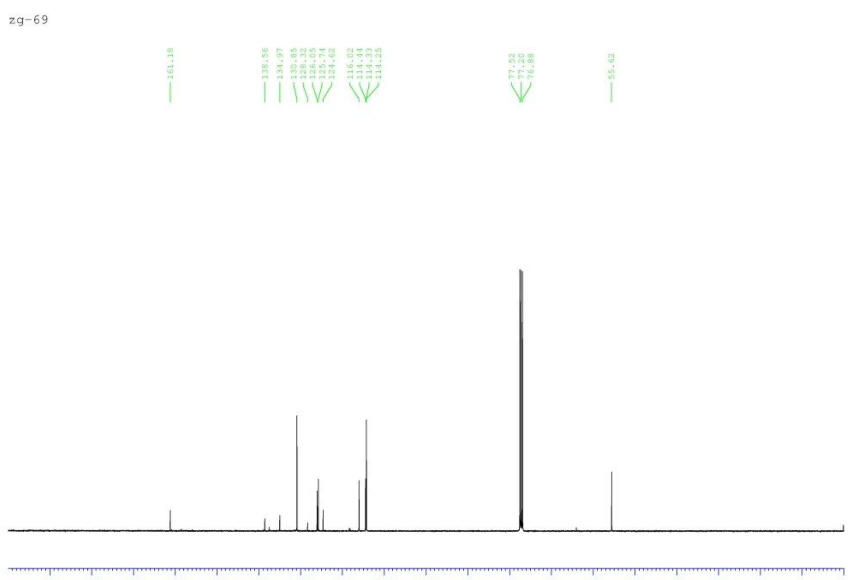
5. 


SZG-25
8.768
8.747
8.094
7.817
7.798
7.750
7.747
7.729
7.711
7.707
7.593
7.591
7.573
7.555
7.553
7.533
7.510
7.496
7.473
7.265
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.00
1.03
1.05
3.07

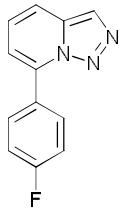

SZG-25
131.96
131.66
130.17
128.44
127.65
127.22
126.80
124.00
116.44
114.85
77.20
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

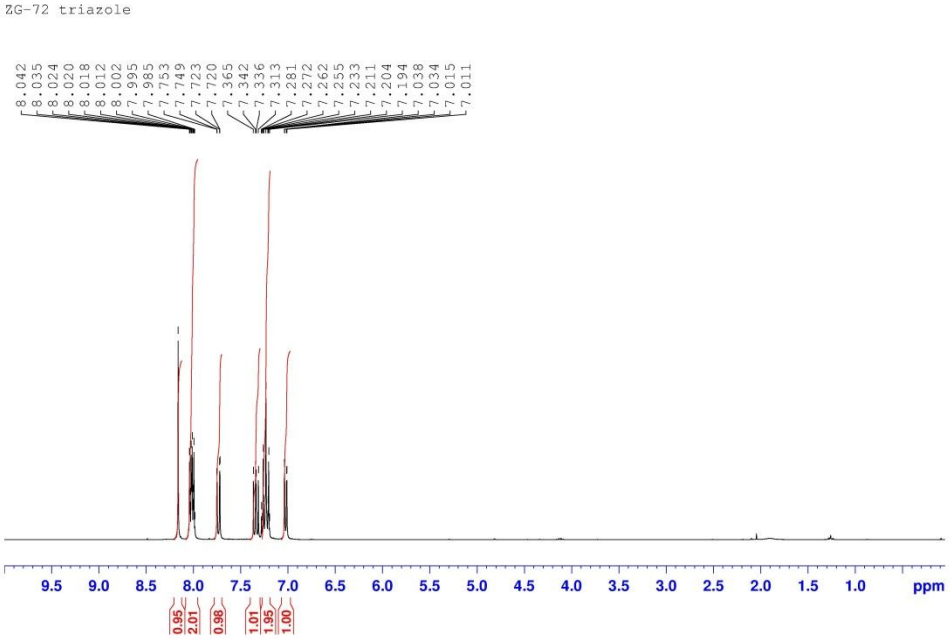
6. 
N
N
N
OMe

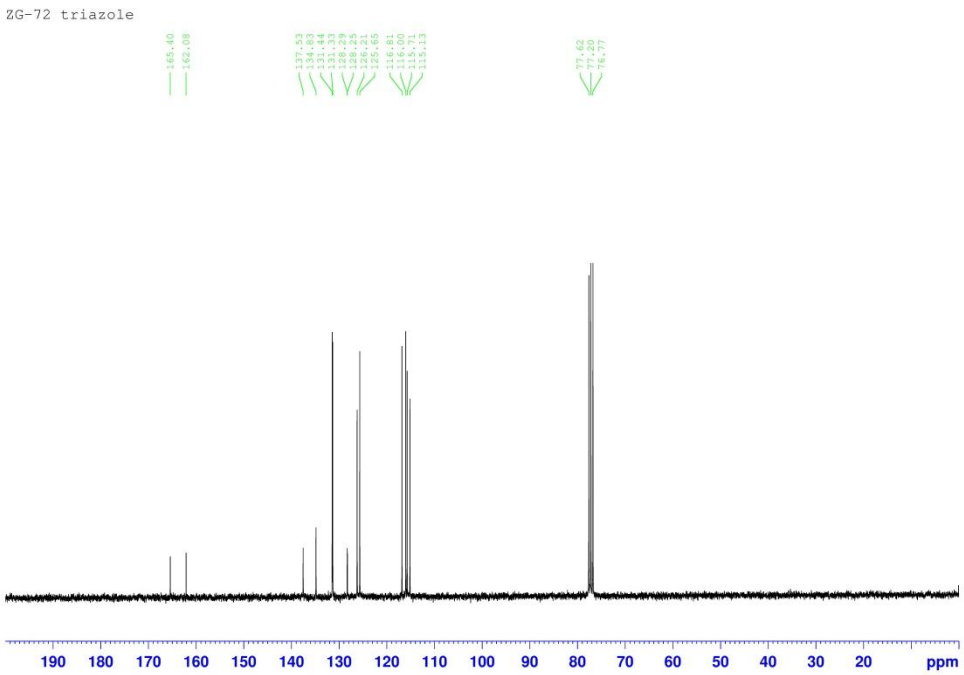

zg-69
8.141
8.002
7.998
7.992
7.985
7.980
7.973
7.691
7.669
7.334
7.317
7.312
7.295
7.260
7.077
7.072
7.059
7.055
7.015
7.013
6.998
3.892
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.94
2.11
1.01
0.99
1.99
1.18
3.00

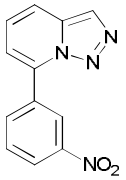

zg-69
161.18
138.56
134.97
130.85
128.32
126.05
125.74
124.62
116.02
114.44
114.33
114.25
77.52
77.20
76.88
55.62
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

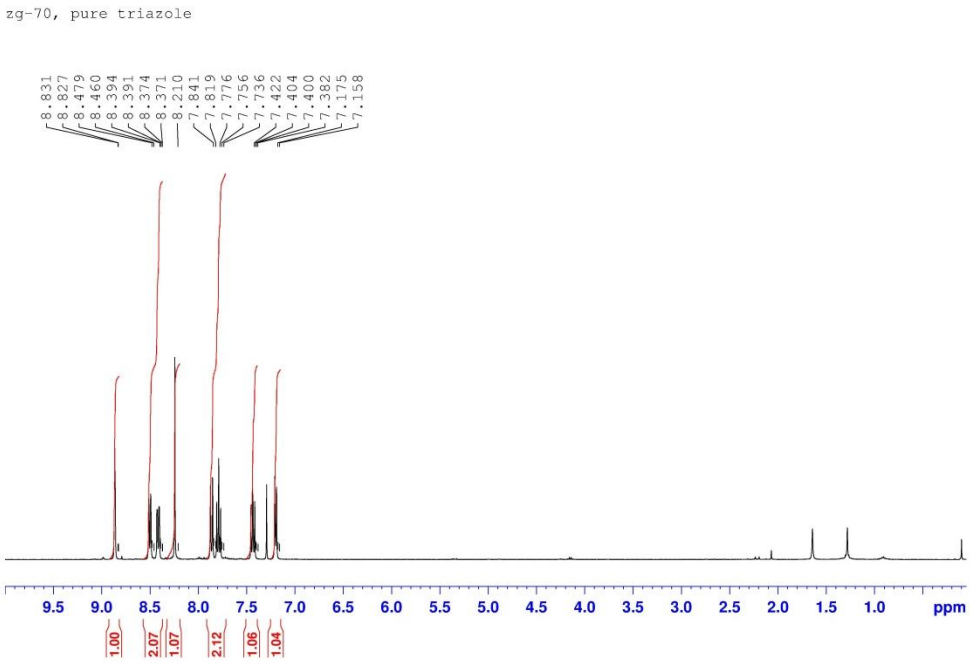
7.

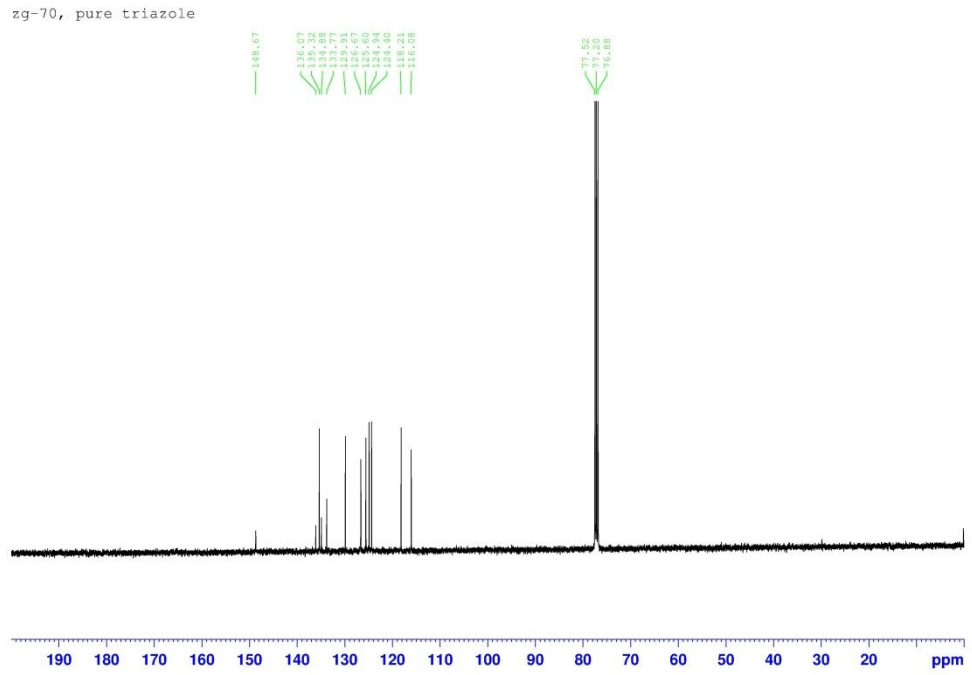

N
N
N
F

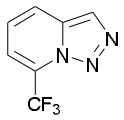

ZG-72 triazole
8.042
8.035
8.024
8.020
8.018
8.012
8.002
7.995
7.985
7.753
7.749
7.723
7.720
7.365
7.342
7.336
7.313
7.281
7.272
7.262
7.255
7.233
7.211
7.204
7.194
7.038
7.034
7.015
7.011
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.95
2.01
0.98
1.01
1.95
1.00


ZG-72 triazole
165.40
162.08
137.53
134.83
134.44
131.34
128.29
128.25
125.61
125.56
116.81
116.00
115.71
115.13
77.62
77.20
76.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

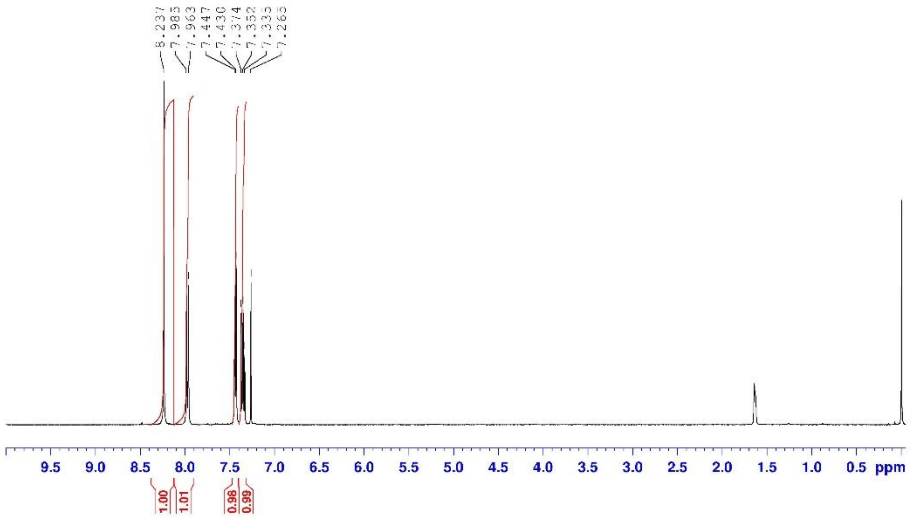
8. 


zg-70, pure triazole
8.831
8.827
8.479
8.460
8.394
8.391
8.374
8.371
8.210
7.841
7.819
7.776
7.756
7.736
7.422
7.404
7.400
7.382
7.175
7.158
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.07
1.07
2.12
1.06
1.04

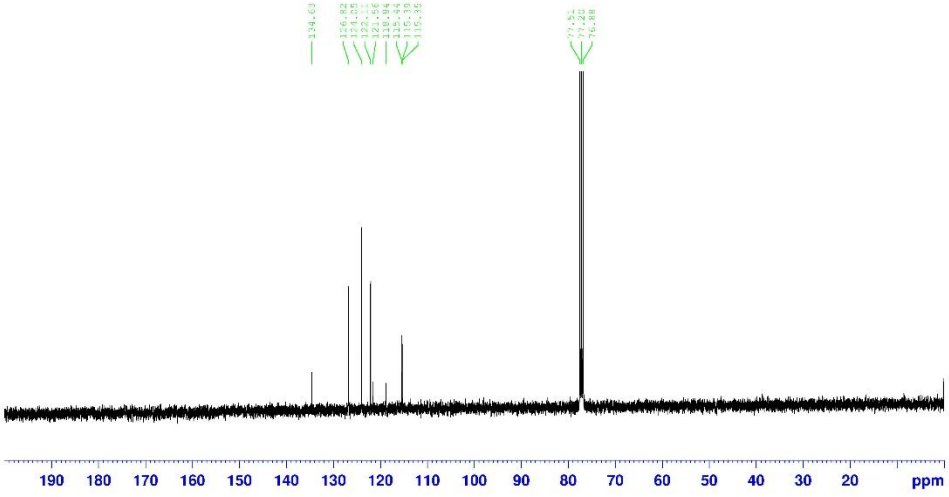

zg-70, pure triazole
148.67
136.67
135.32
134.88
133.77
133.31
126.67
125.60
124.94
124.40
118.21
116.08
77.52
77.20
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

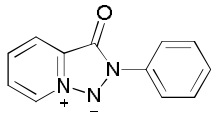
9. 

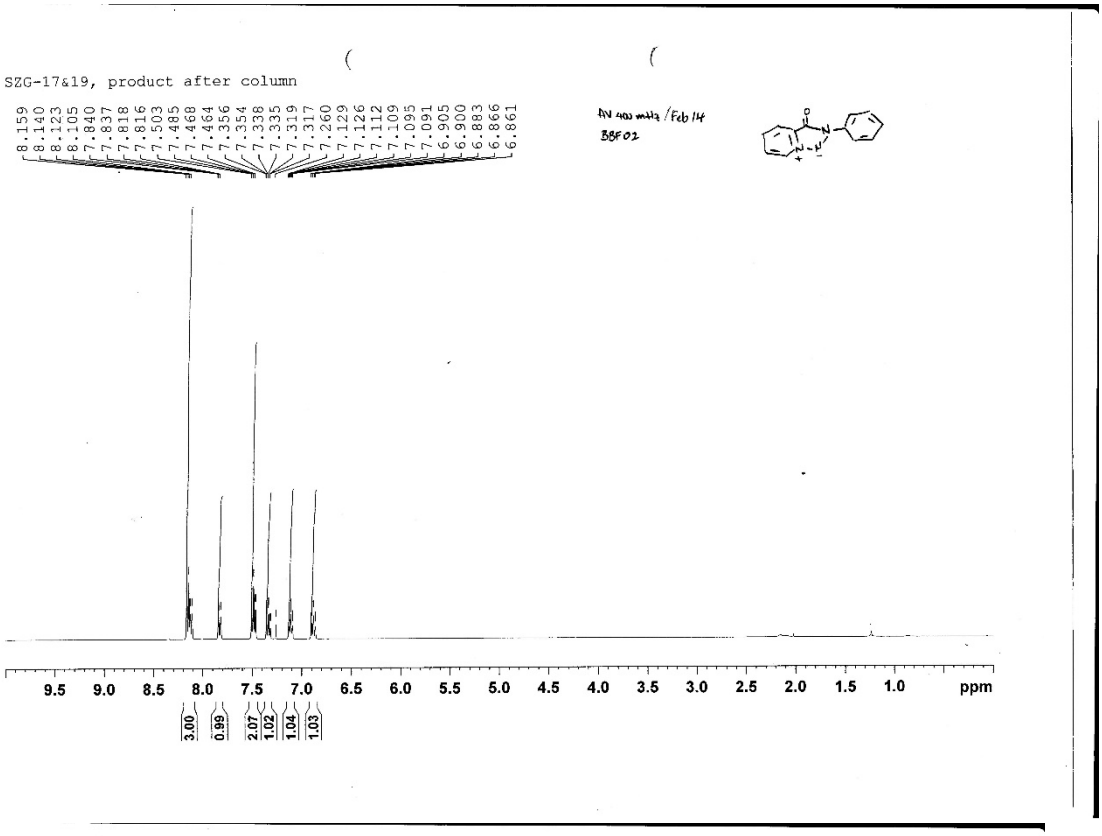
SZG 29, repeat with MnO2, purified product

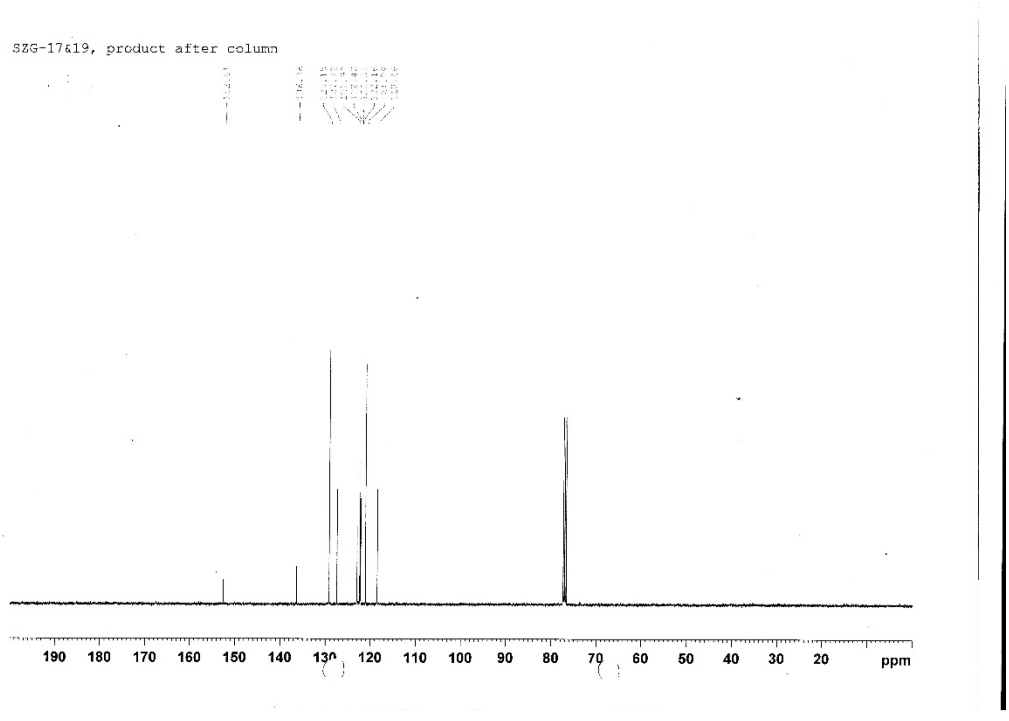


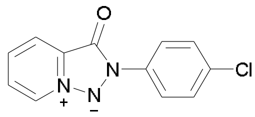
SZG-29, repeat with MnO2, purified product

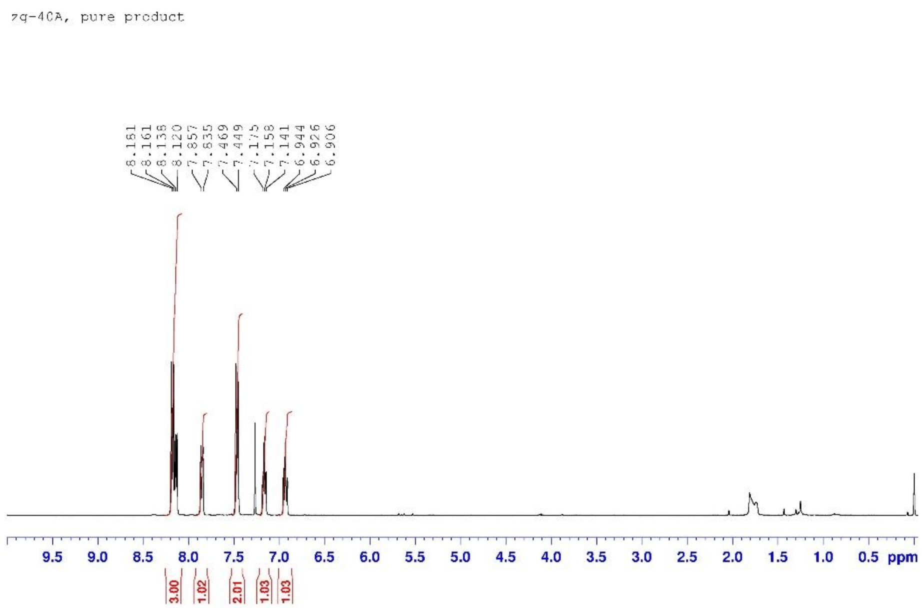


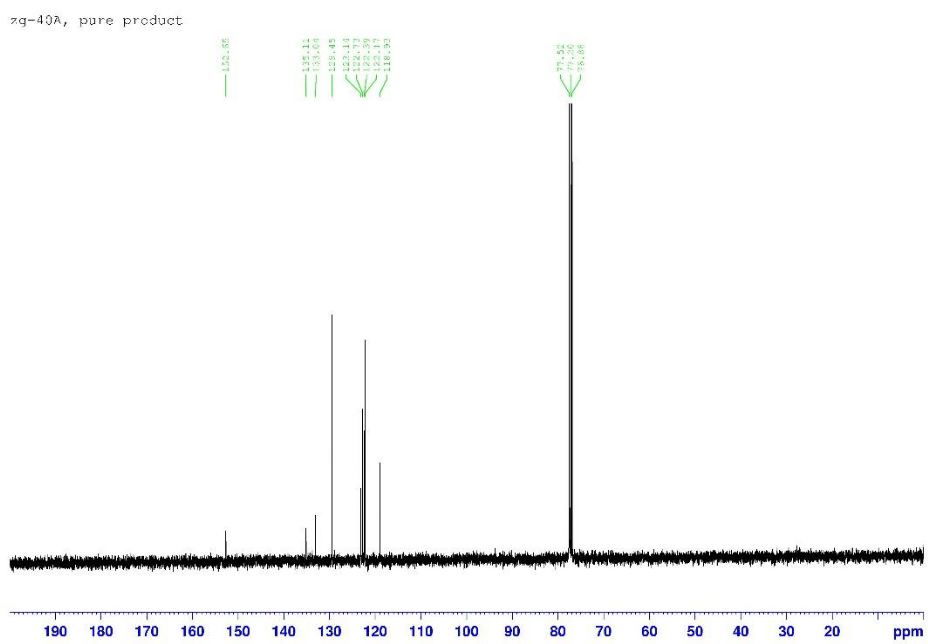
10. 

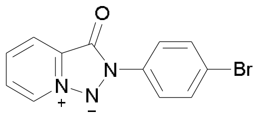

SZG-17&19, product after column
8.159
8.140
8.123
8.105
7.840
7.837
7.818
7.816
7.503
7.485
7.468
7.464
7.356
7.354
7.338
7.335
7.319
7.317
7.260
7.129
7.126
7.112
7.109
7.095
7.091
6.905
6.900
6.883
6.866
6.861
AV 400 MHz / Feb 14
BBF02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.00
0.99
2.07
1.02
1.04
1.03

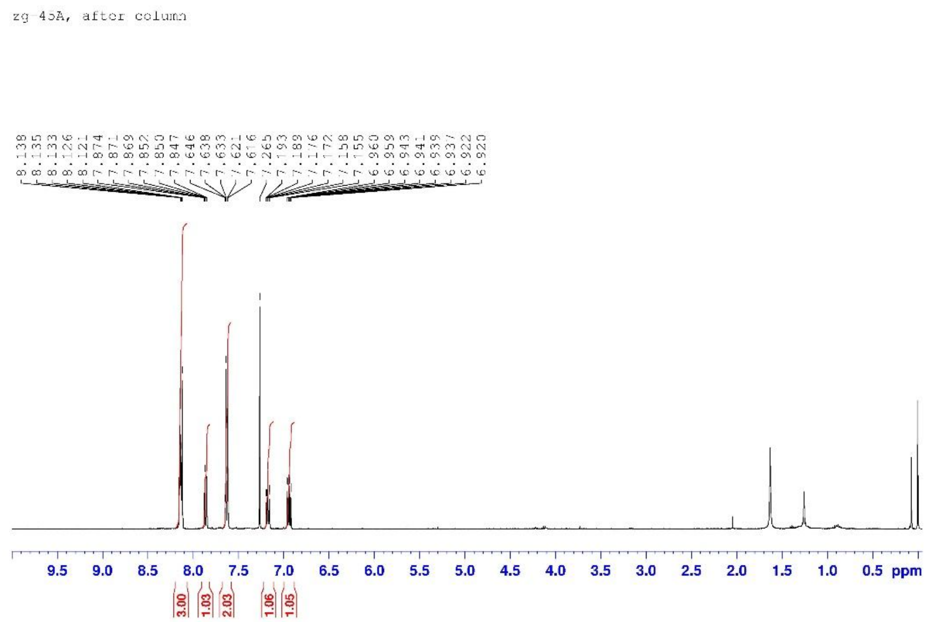

SZG-17&19, product after column
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

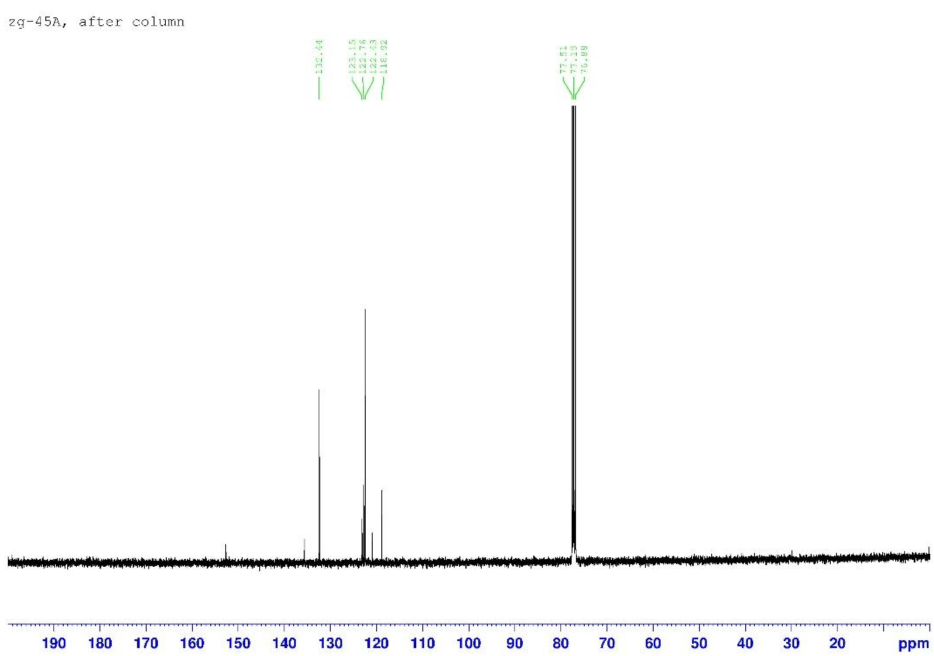
11. 
O
N
N
N
+
−
Cl

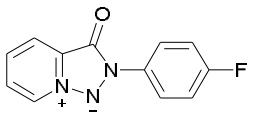

zq-40A, pure product
8.161
8.161
8.138
8.120
7.857
7.835
7.469
7.449
7.175
7.158
7.141
6.944
6.926
6.906
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.00
1.02
2.01
1.03
1.03


zq-40A, pure product
152.65
135.11
133.04
129.45
123.14
122.73
122.39
122.17
118.93
77.52
77.20
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

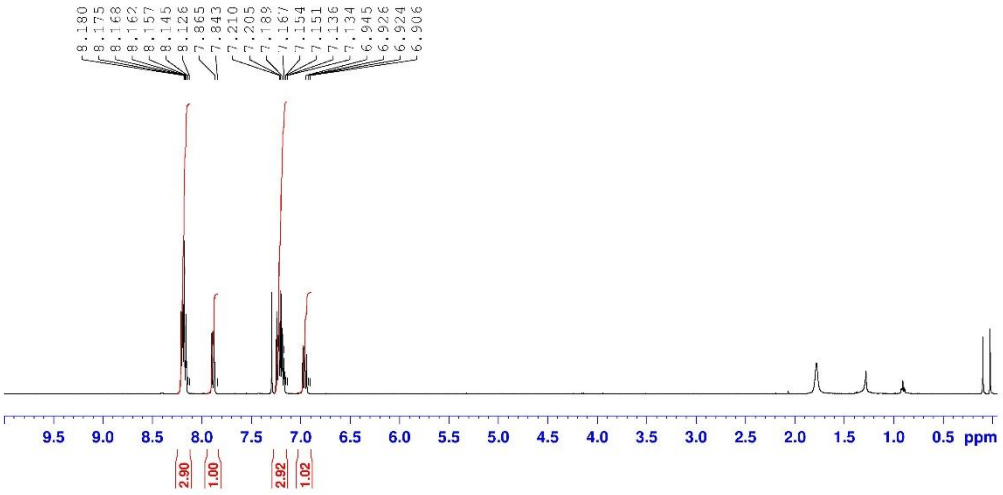
12. 
O
N
Br
N
N
+
–


zg-45A, after column
8.138
8.135
8.133
8.126
8.121
7.874
7.871
7.869
7.852
7.850
7.847
7.646
7.638
7.633
7.621
7.616
7.265
7.193
7.189
7.176
7.172
7.158
7.155
6.960
6.959
6.943
6.941
6.939
6.937
6.922
6.920
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.00
1.03
2.03
1.06
1.05

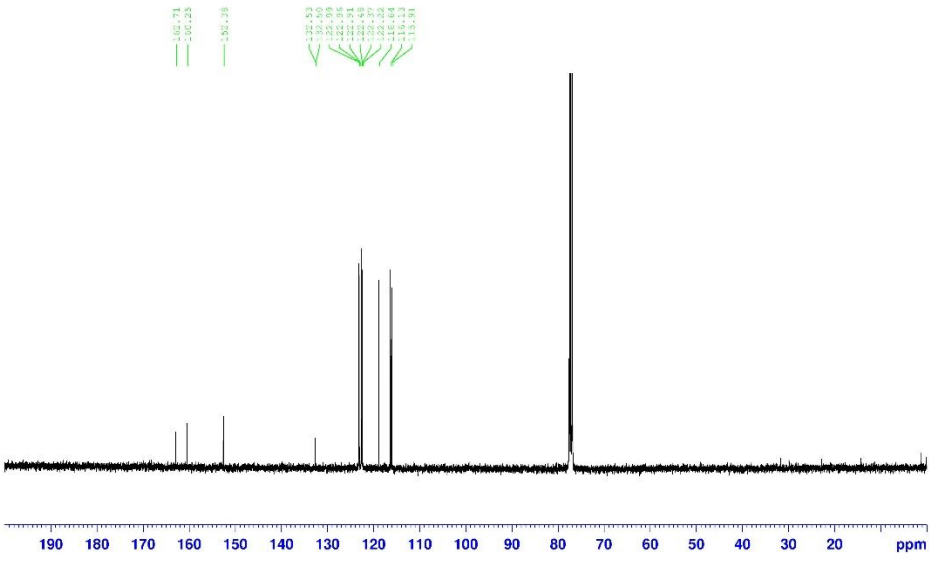

zg-45A, after column
132.44
123.15
122.76
122.43
118.92
77.51
77.19
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

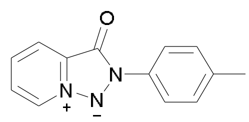
13. 

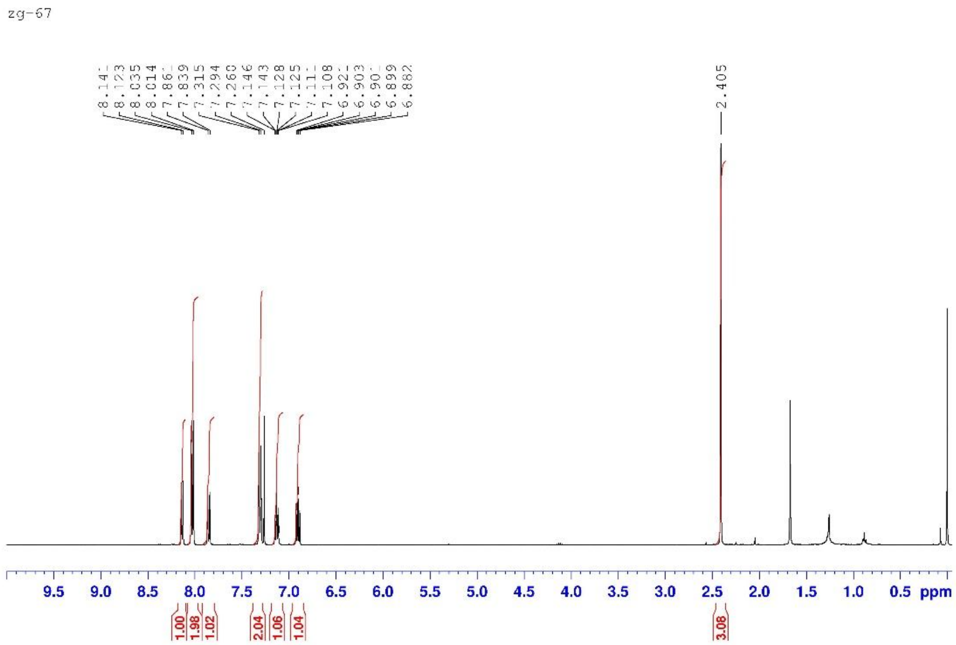
zg 57A, the product

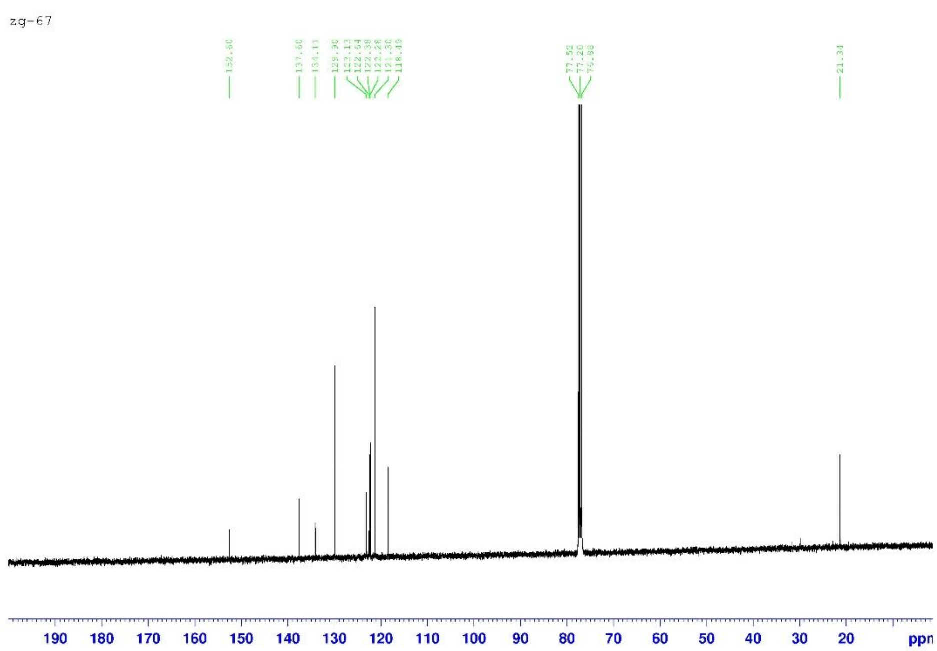


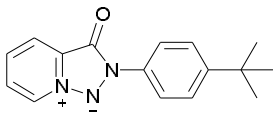
zg-57A, the product

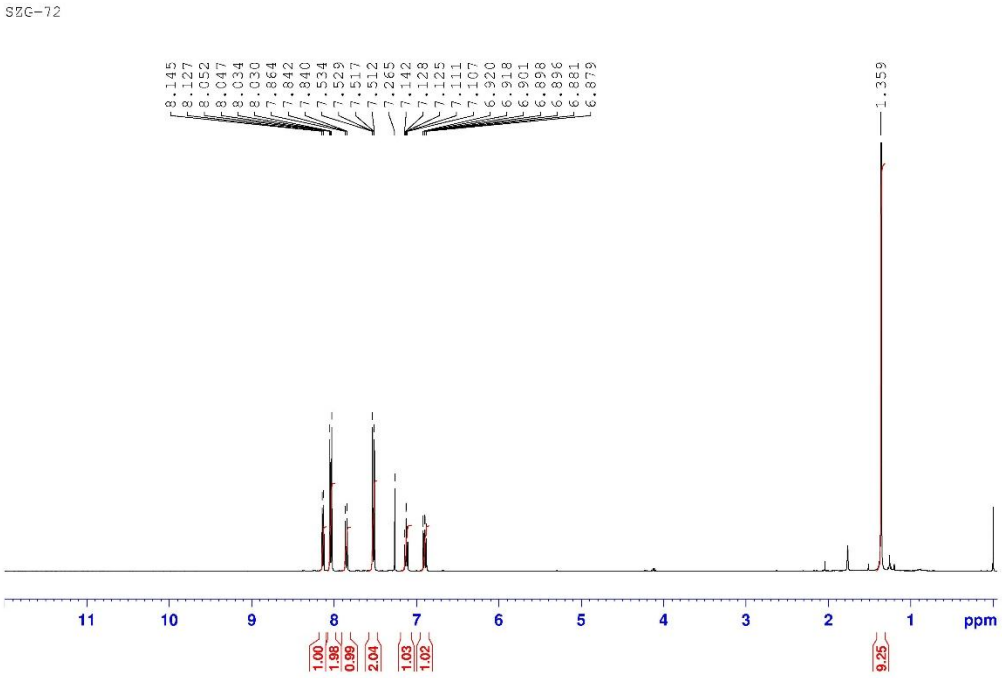


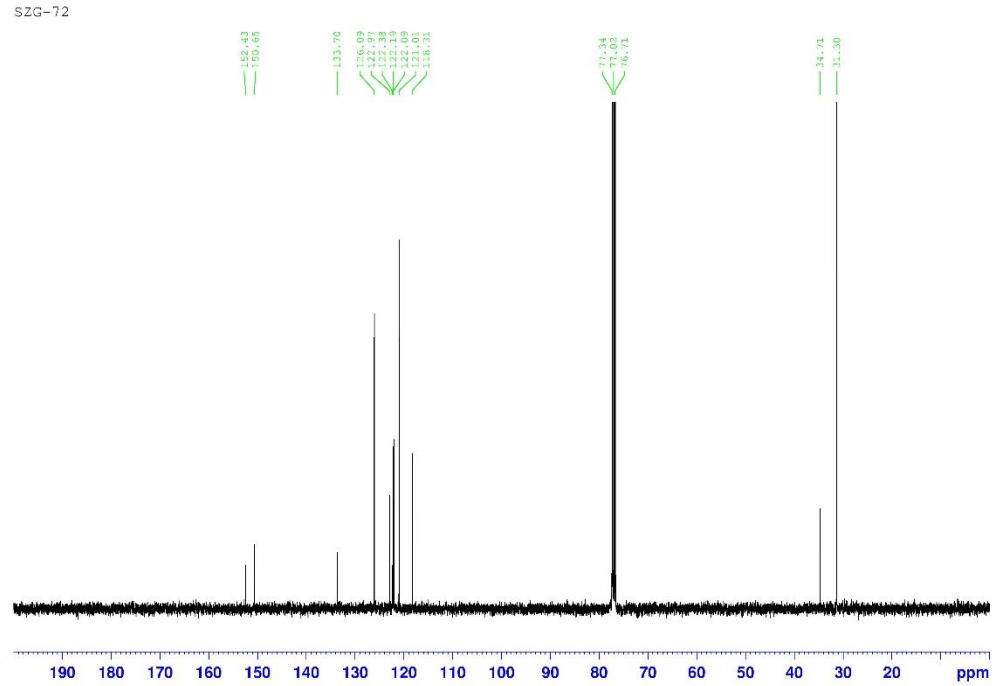
14. 

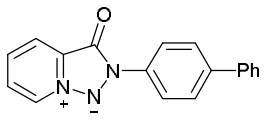

zg-67
2.405
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.98
1.02
2.04
1.06
1.04
3.08

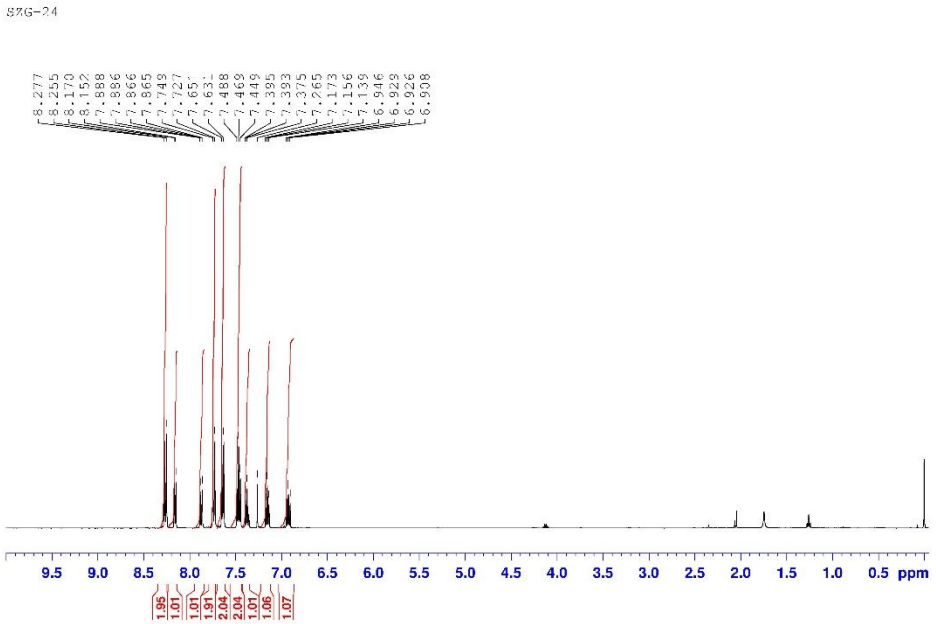

zg-67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

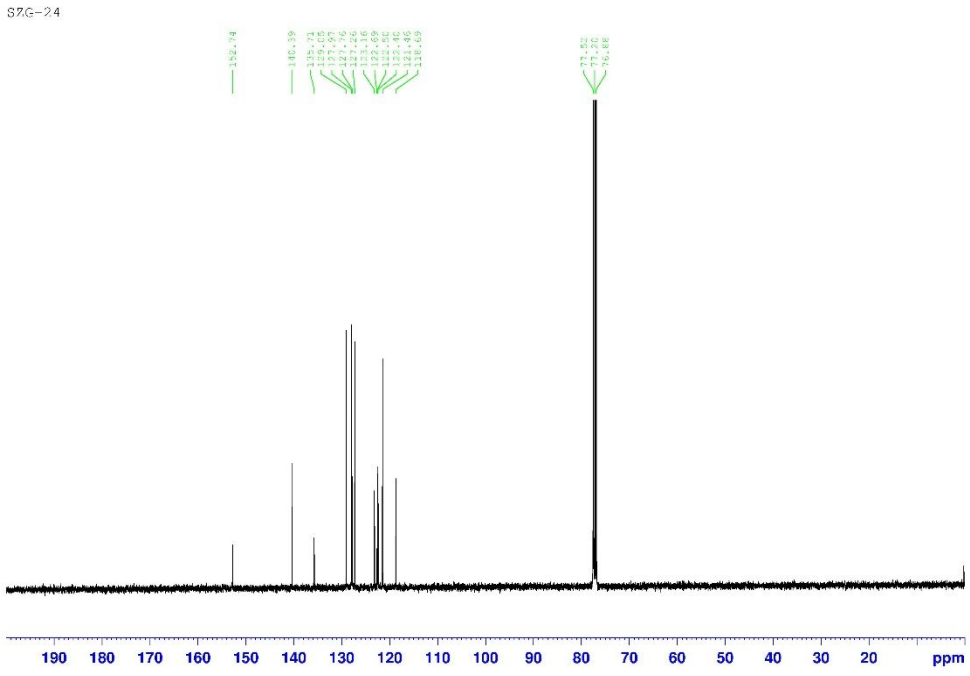
15. 

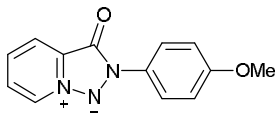

SZG-72
8.145
8.127
8.052
8.047
8.034
8.030
7.864
7.842
7.840
7.534
7.529
7.517
7.512
7.265
7.142
7.128
7.125
7.111
7.107
6.920
6.918
6.901
6.898
6.896
6.881
6.879
1.359
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.98
0.99
2.04
1.03
1.02
9.25

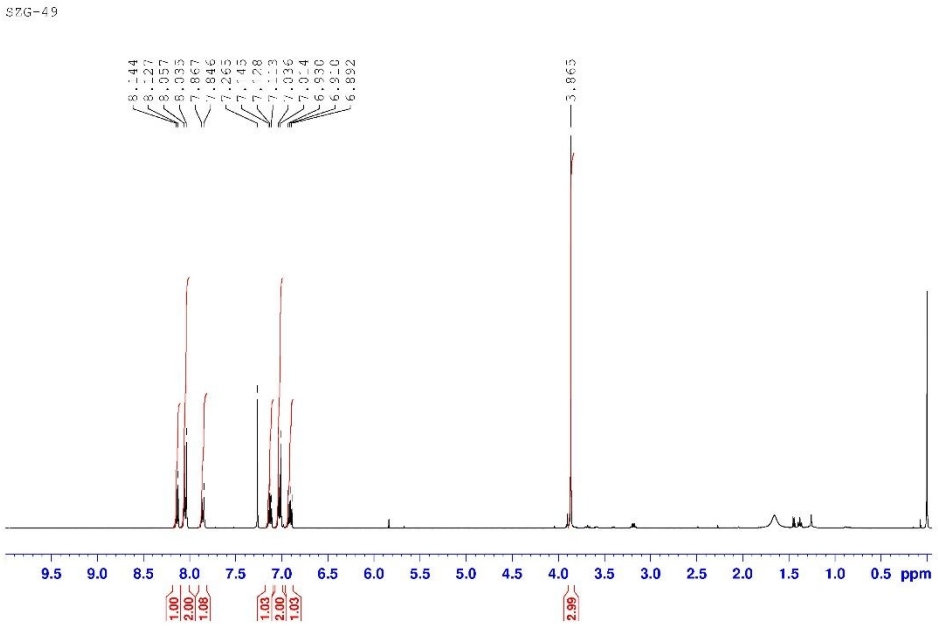

SZG-72
152.43
150.65
133.70
126.09
122.97
122.38
122.19
121.89
121.01
116.31
77.34
77.02
76.71
34.71
31.30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

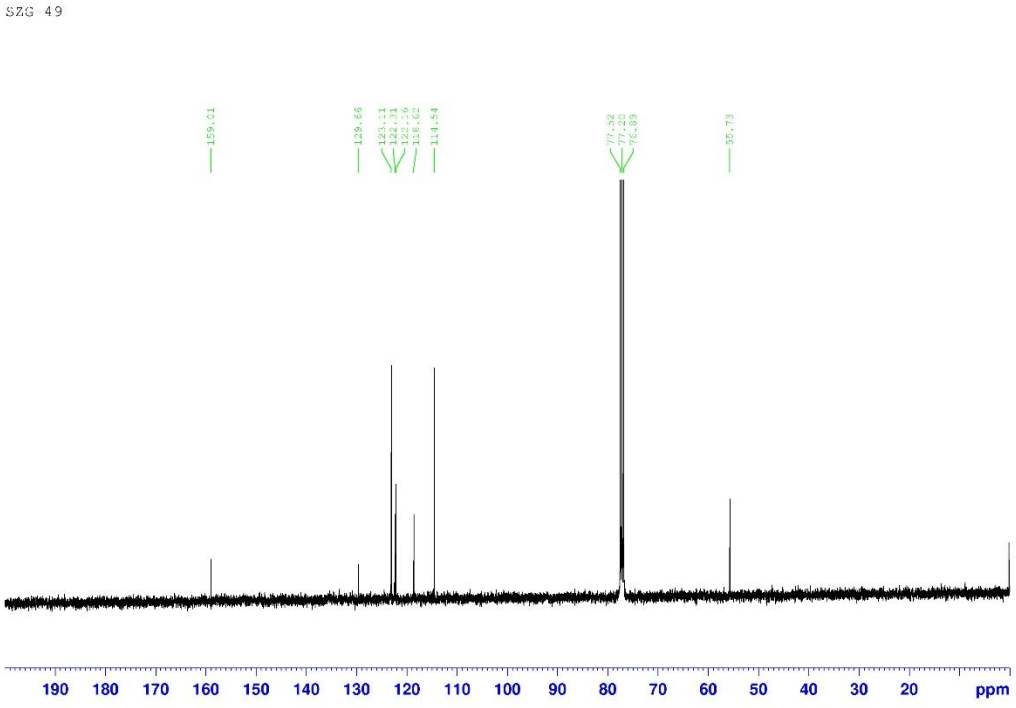
16. 
O
N
N
Ph

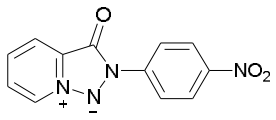

SZG-24
8.277
8.255
8.170
8.152
7.888
7.886
7.866
7.865
7.749
7.727
7.488
7.469
7.449
7.395
7.393
7.375
7.265
7.173
7.156
7.139
6.946
6.929
6.926
6.908
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.95
1.01
1.01
1.91
2.04
2.04
1.01
1.06
1.07

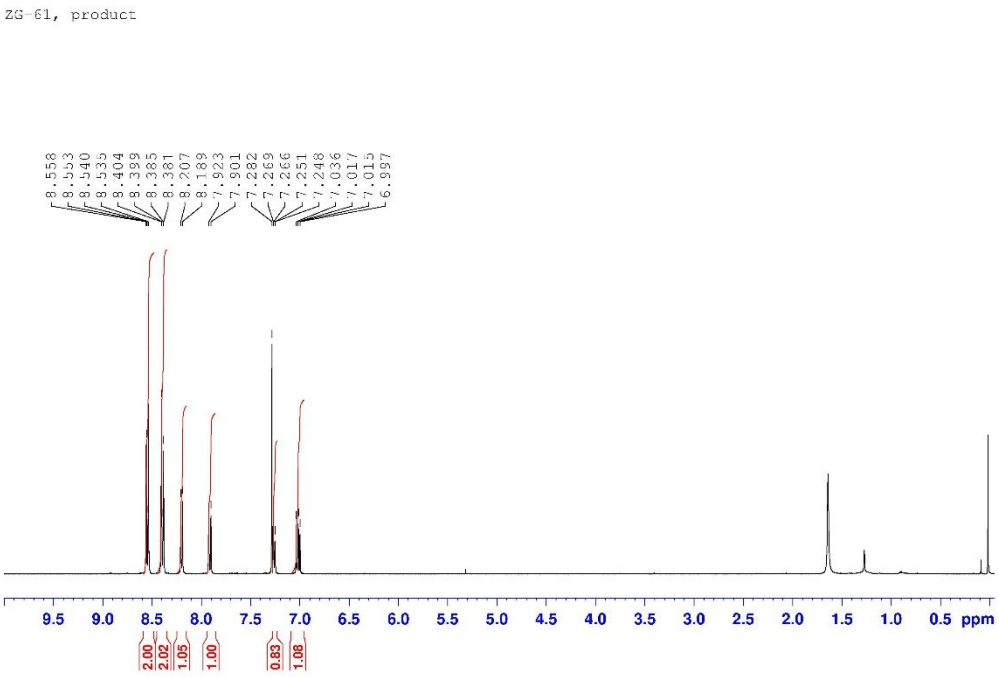

SZG-24
152.74
140.39
135.71
129.05
127.97
125.76
123.16
122.69
77.52
77.20
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

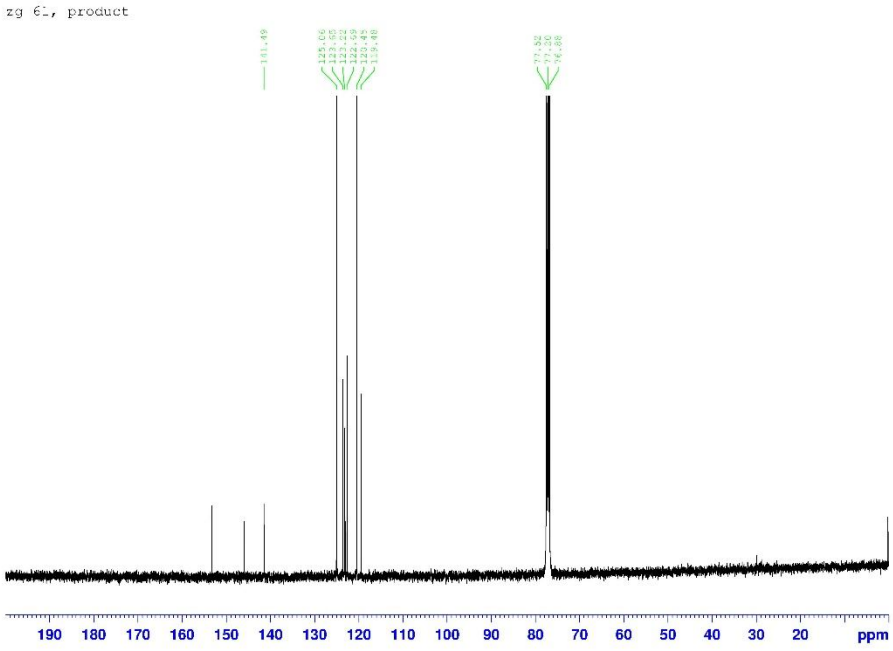
17. 
O
N
N
+
-
OMe

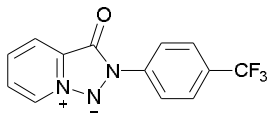

SZG-49
8.144
8.127
8.057
8.035
7.867
7.846
7.265
7.145
7.128
7.113
7.036
7.014
6.930
6.910
6.892
3.865
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.00
1.08
1.03
2.00
1.03
2.99


SZG 49
159.01
129.66
123.11
122.31
121.76
114.62
114.54
77.32
77.20
76.89
55.73
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

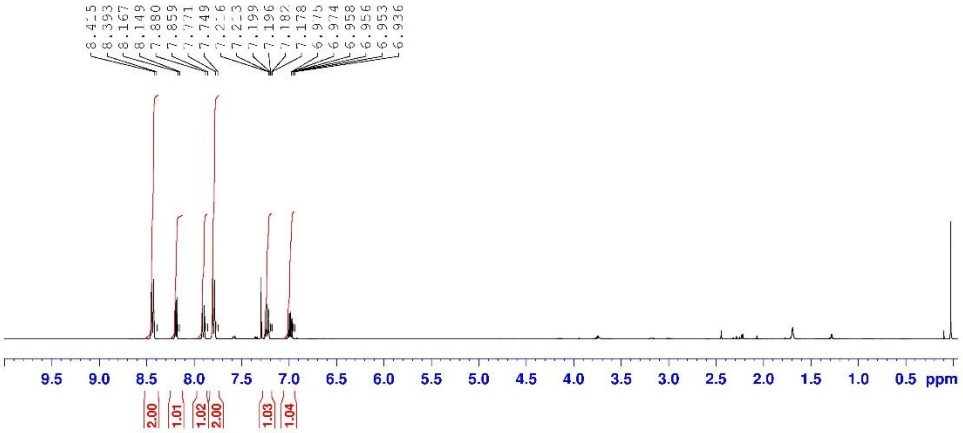
18. 


ZG-61, product
8.558
8.553
8.540
8.535
8.404
8.399
8.385
8.381
8.207
8.189
7.923
7.901
7.282
7.269
7.266
7.251
7.248
7.036
7.017
7.015
6.997
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.02
1.05
1.00
0.83
1.08

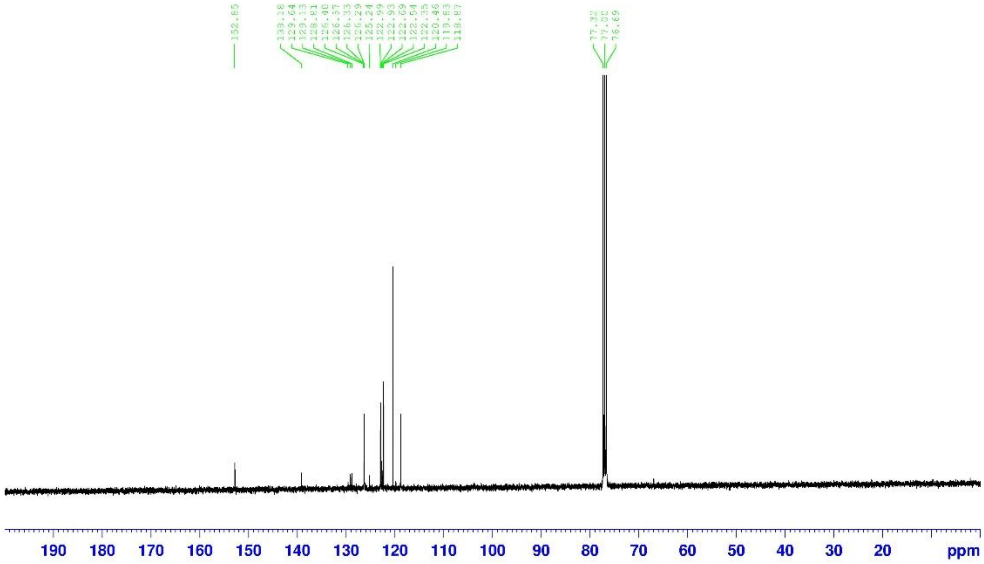

zg 61, product
141.49
125.06
123.65
123.22
122.99
120.45
119.40
77.32
77.00
76.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

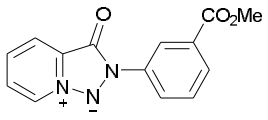
19. 

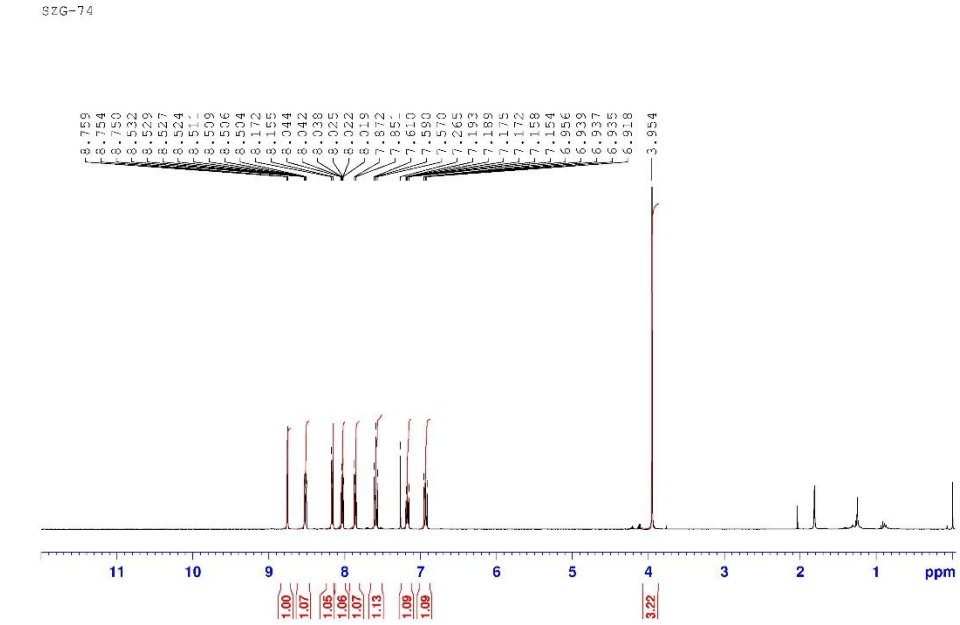
zg-63A, product

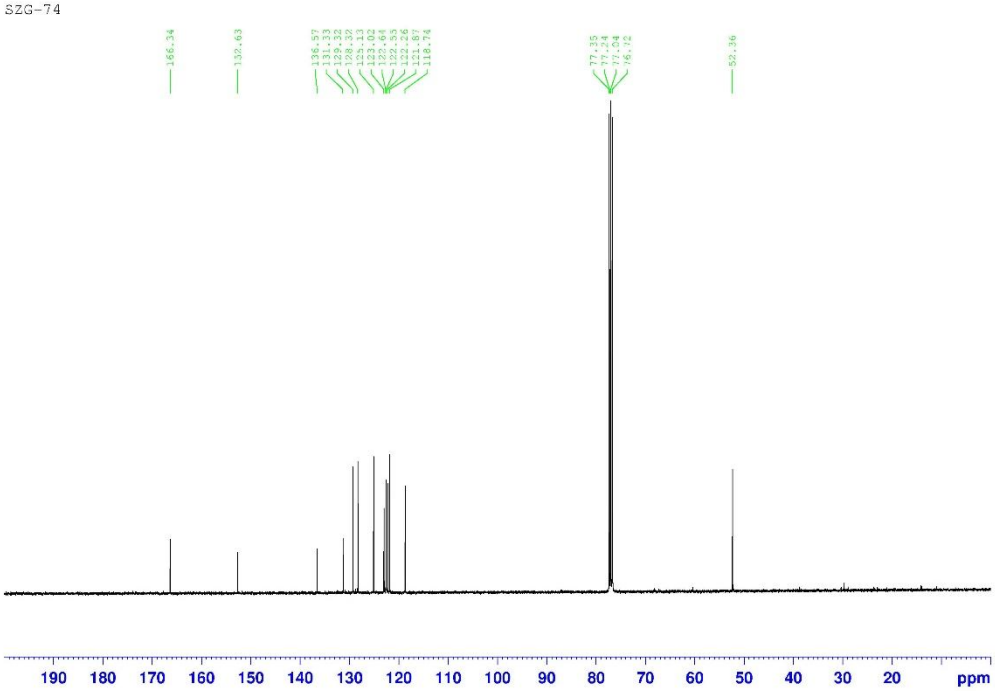


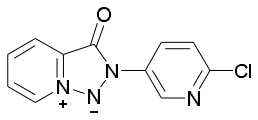
zg-63A, product

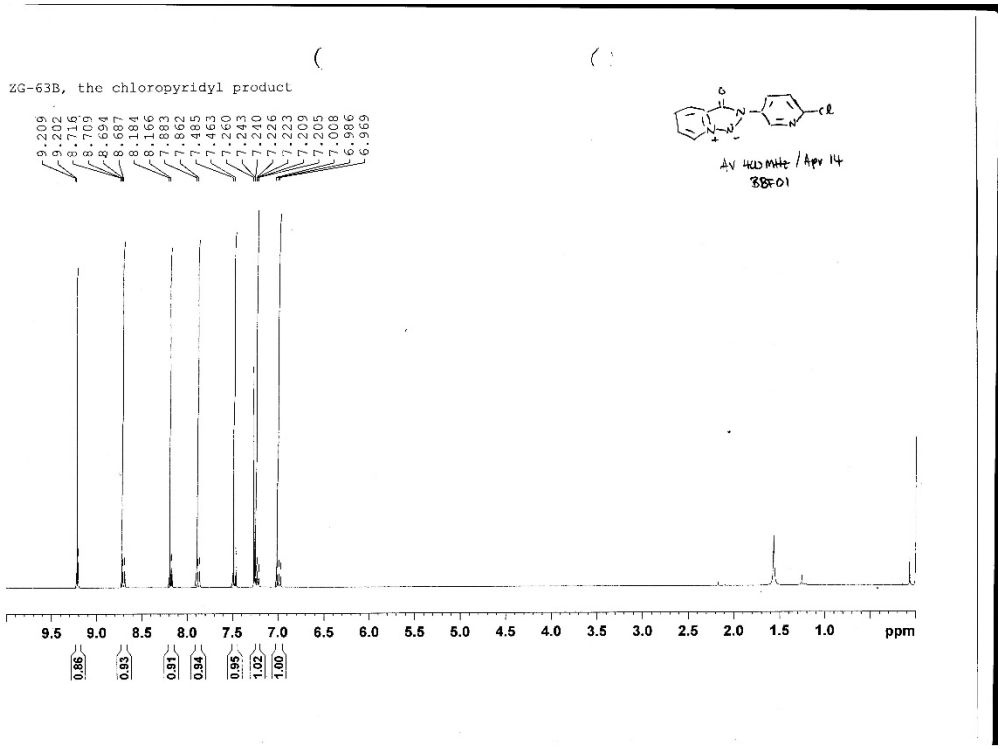


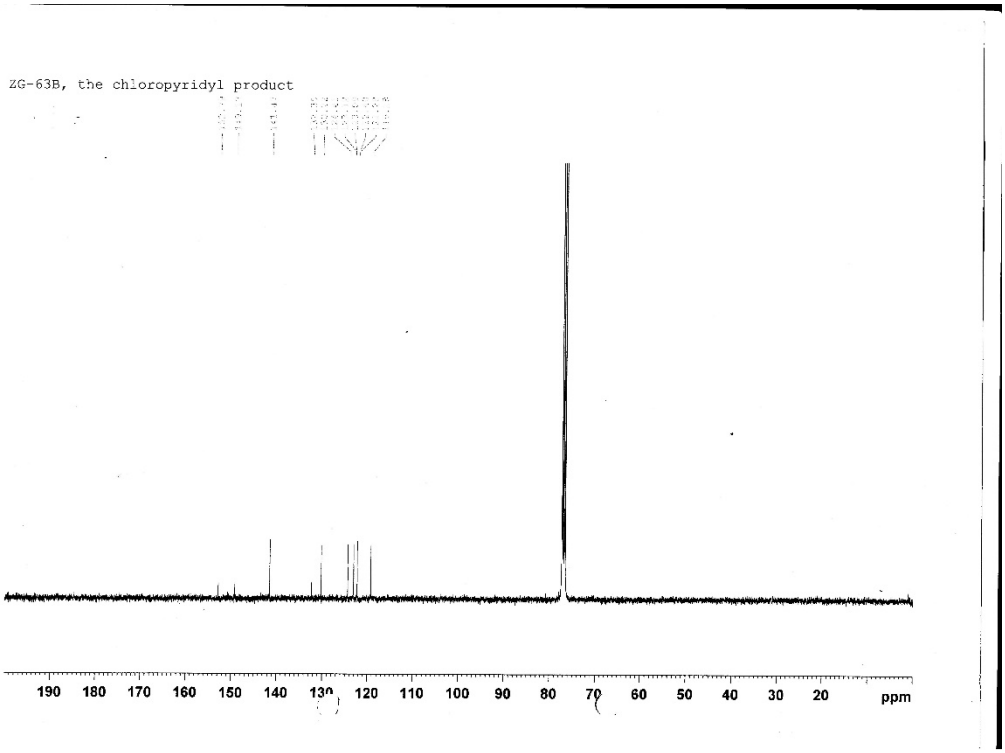
20. 
O
CO2Me
N
N
+
-

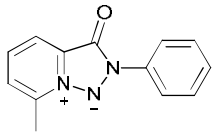

SZG-74
8.759
8.754
8.750
8.532
8.529
8.527
8.524
8.509
8.506
8.504
8.172
8.155
8.044
8.042
8.038
8.025
8.022
8.019
7.872
7.610
7.590
7.570
7.265
7.193
7.189
7.175
7.172
7.158
7.154
6.956
6.939
6.937
6.935
6.918
3.954
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.07
1.05
1.06
1.07
1.13
1.09
1.09
3.22

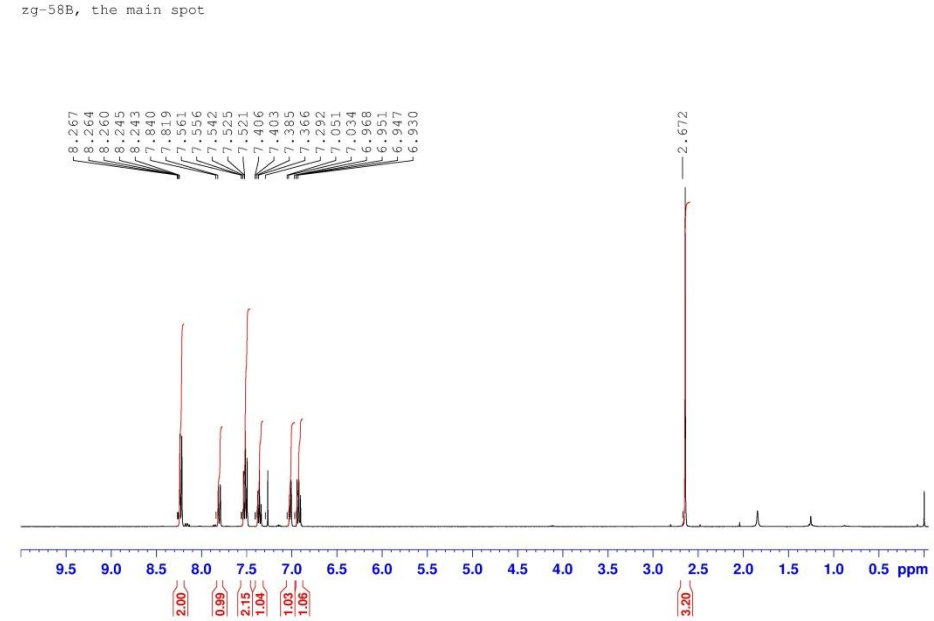

SZG-74
166.34
132.63
136.57
131.33
129.32
128.32
125.13
123.02
122.64
122.53
122.26
121.67
118.74
77.35
77.24
77.04
76.72
52.36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

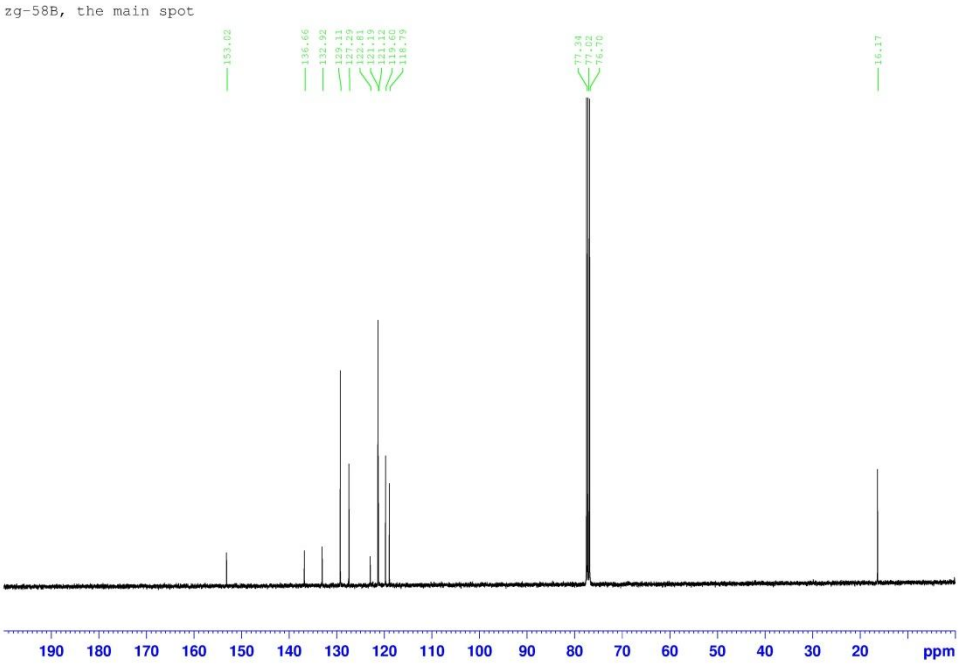
21. 

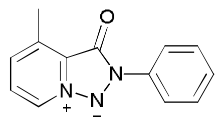

ZG-63B, the chloropyridyl product
9.209
9.202
8.716
8.709
8.694
8.687
8.184
8.166
7.883
7.862
7.485
7.463
7.260
7.243
7.240
7.226
7.223
7.209
7.205
7.008
6.986
6.969
AV 400 MHz / Apr 14
BBF01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.86
0.93
0.91
0.94
0.95
1.02
1.00

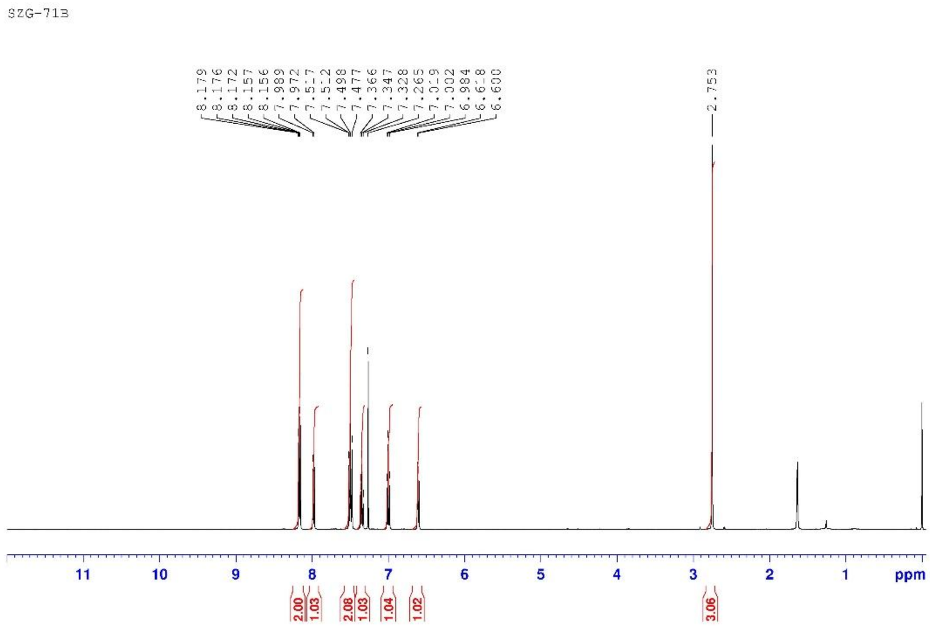

ZG-63B, the chloropyridyl product
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

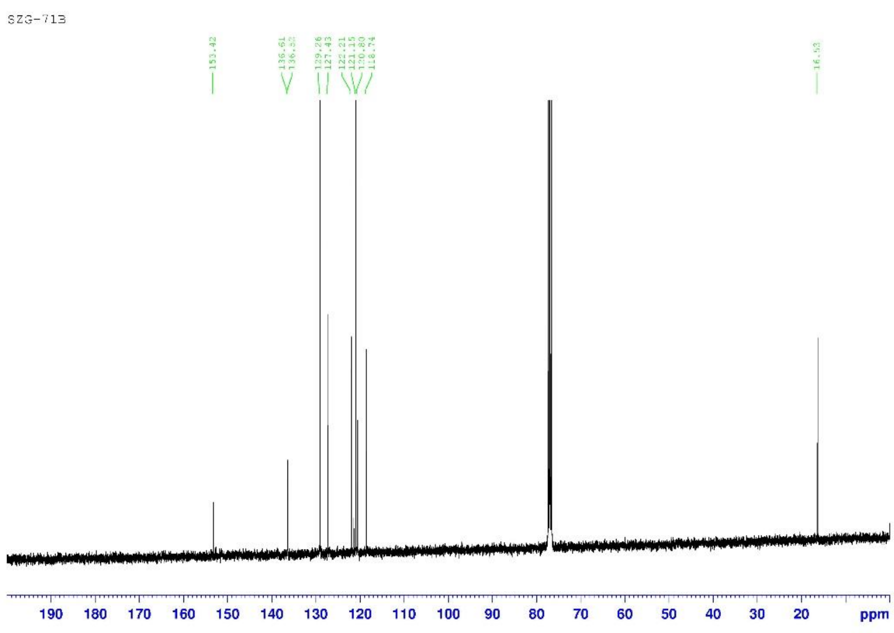
22. 

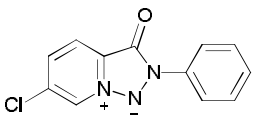

zg-58B, the main spot
8.267
8.264
8.260
8.245
8.243
7.840
7.819
7.561
7.556
7.542
7.525
7.521
7.406
7.403
7.385
7.366
7.292
7.051
7.034
6.968
6.951
6.947
6.930
2.672
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
0.99
2.15
1.04
1.03
1.06
3.20

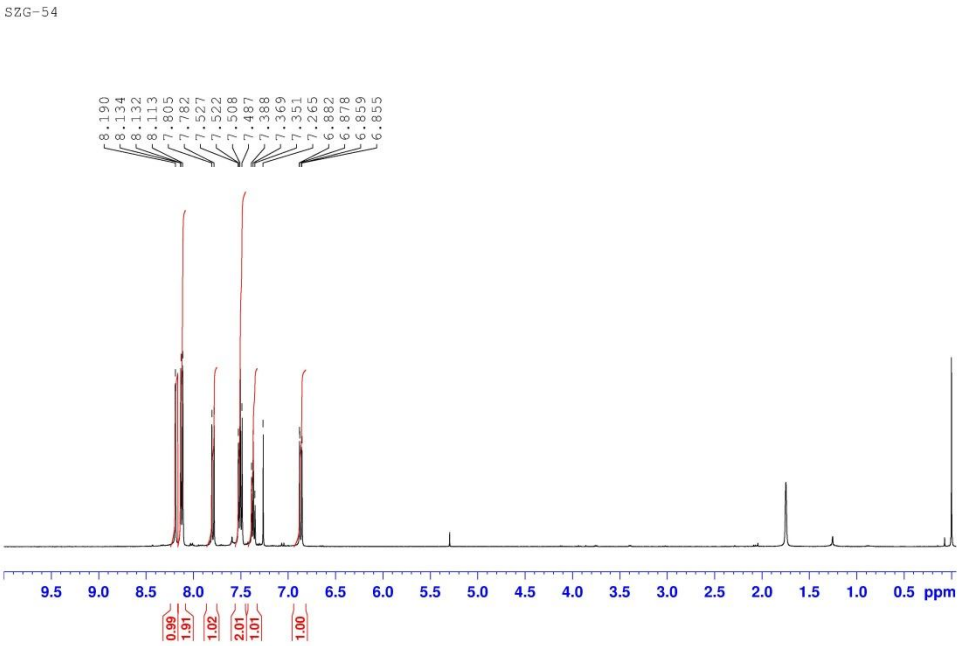

zg-58B, the main spot
153.02
136.66
132.92
129.11
127.29
125.31
121.19
121.12
119.60
118.79
77.34
77.02
76.70
16.17
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

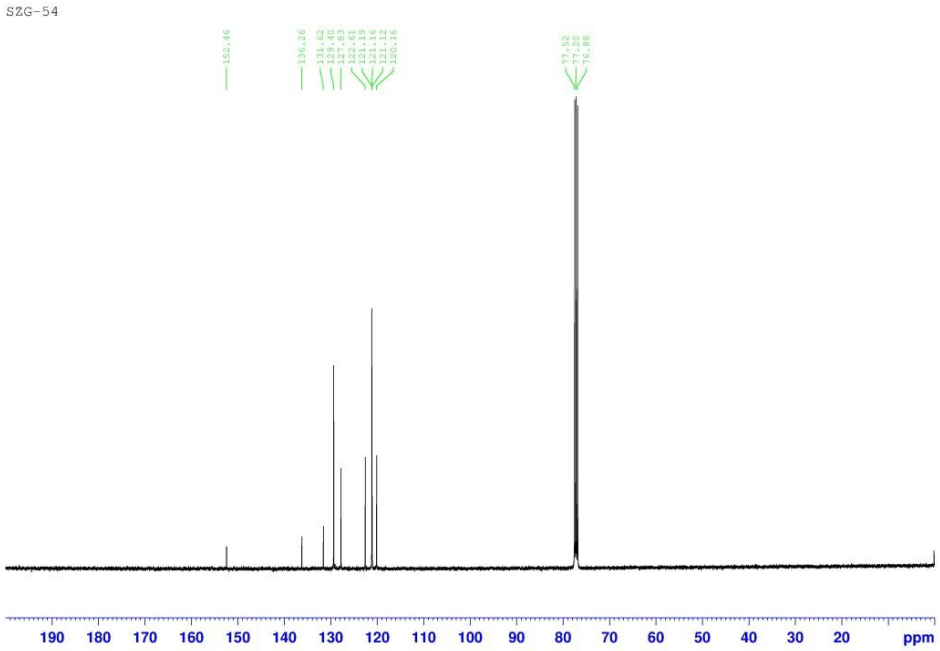
23. 

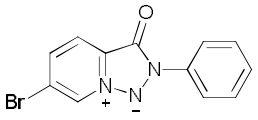

SZG-71B
8.179
8.176
8.172
8.157
8.156
7.989
7.972
7.517
7.512
7.498
7.477
7.366
7.347
7.328
7.265
7.319
7.002
6.984
6.618
6.600
2.753
ppm
2.00
1.03
2.08
1.03
1.04
1.02
3.06

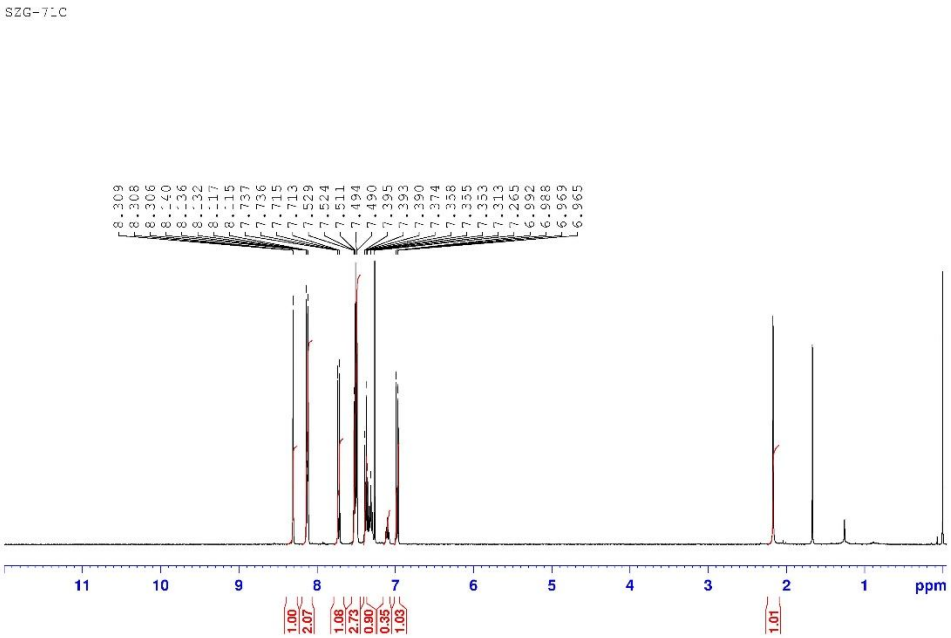

SZG-71B
153.42
136.61
136.55
129.26
127.43
122.21
121.15
120.80
118.74
16.53
ppm

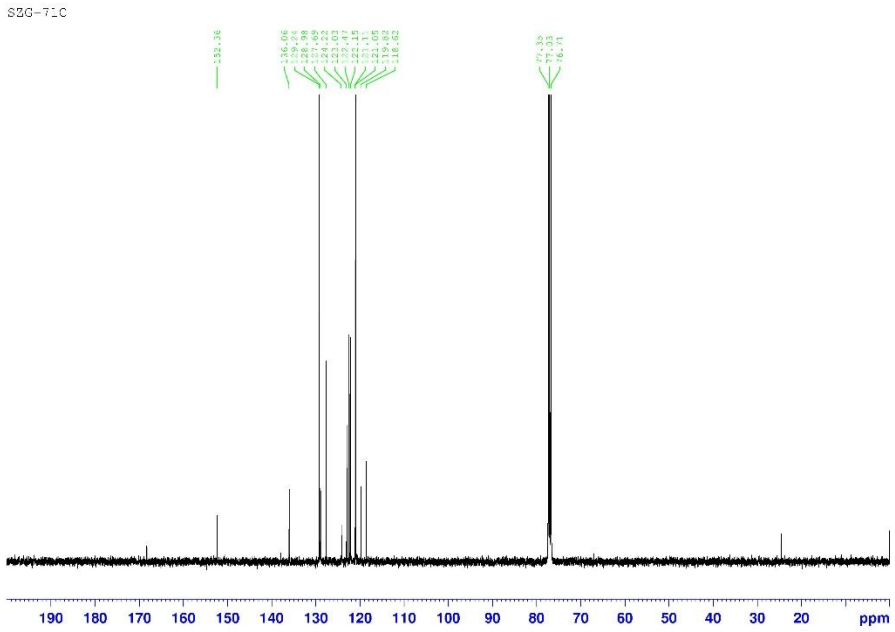
24. 

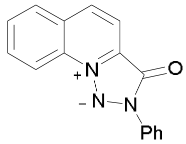

SZG-54
8.190
8.134
8.132
8.113
7.805
7.782
7.527
7.522
7.508
7.487
7.388
7.369
7.351
7.265
6.882
6.878
6.859
6.855
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99
1.91
1.02
2.01
1.01
1.00

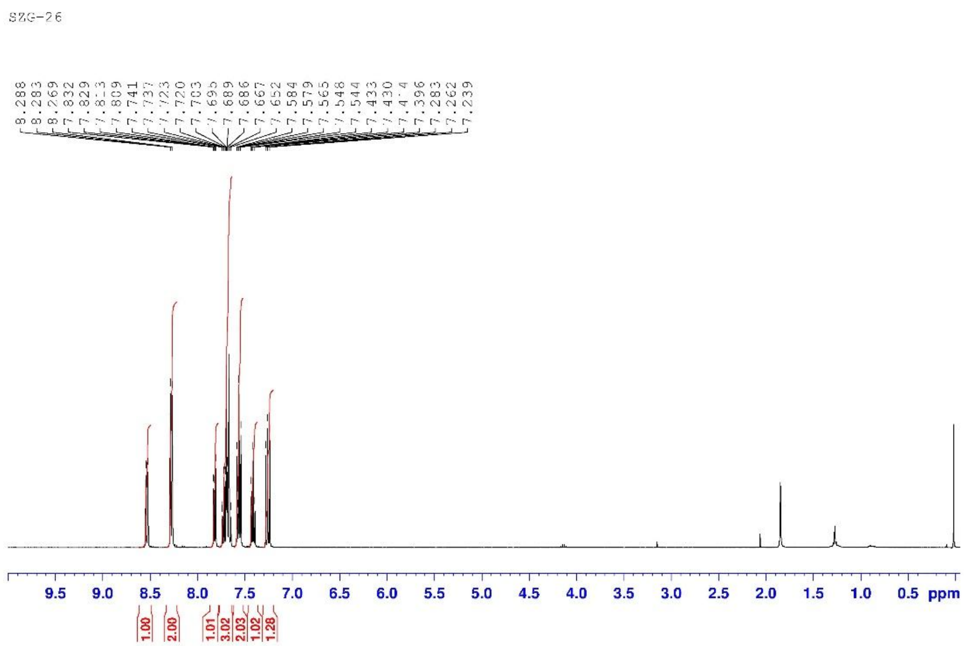

SZG-54
152.46
136.26
131.62
129.40
127.83
125.61
121.19
121.16
121.12
120.16
77.52
77.20
76.88
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

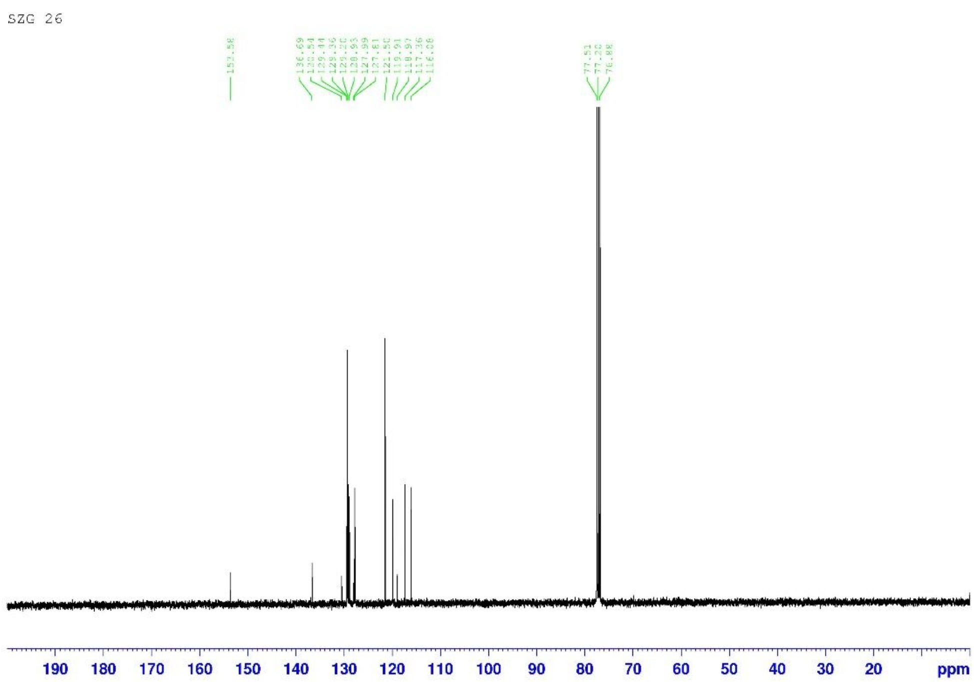
25. 

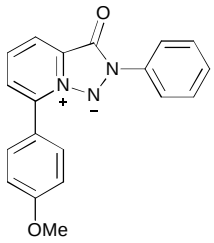

SZG-7LC
8.309
8.308
8.306
8.140
8.136
8.132
8.117
8.115
7.737
7.736
7.715
7.713
7.529
7.524
7.511
7.494
7.490
7.395
7.393
7.390
7.374
7.358
7.335
7.353
7.313
7.265
6.992
6.988
6.969
6.965
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.07
1.08
2.73
0.90
0.35
1.03
1.01

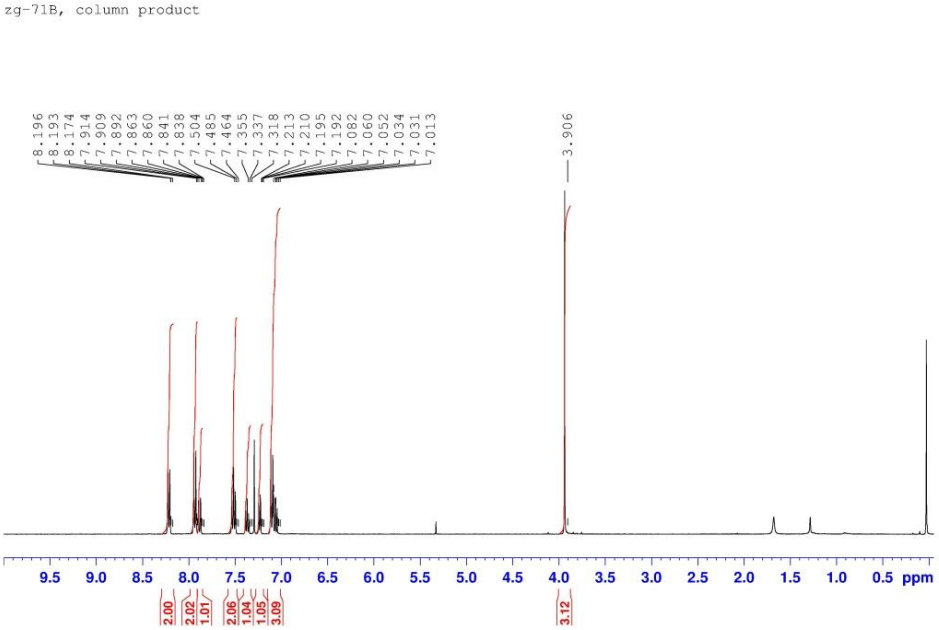

SZG-7LC
152.36
136.06
128.98
127.69
124.03
123.03
122.47
122.15
121.11
121.05
119.82
116.82
77.33
77.03
76.71
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

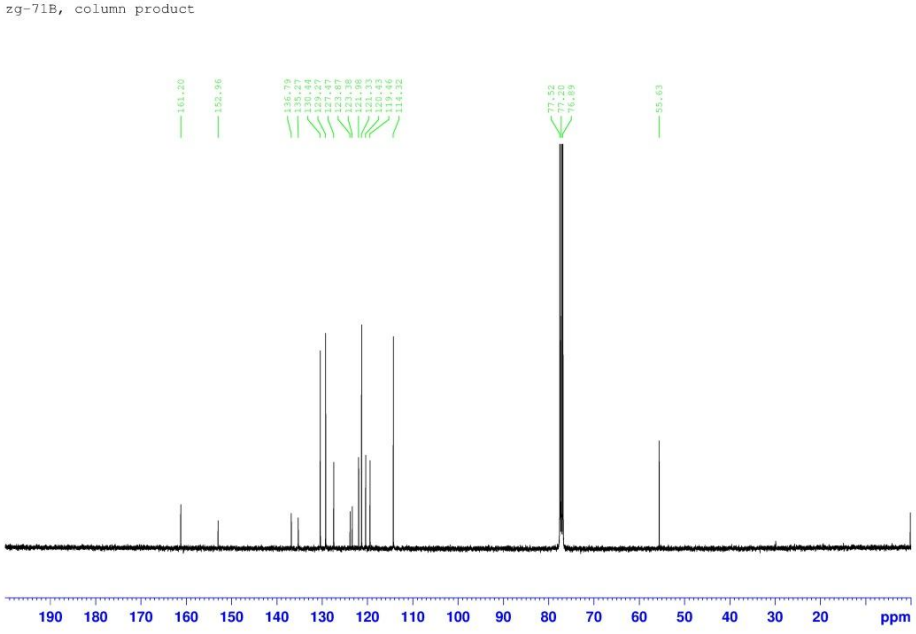
26. 

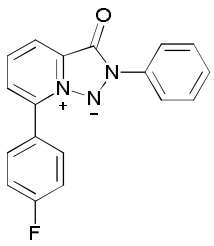

SZG-26
8.288
8.283
8.269
7.832
7.829
7.813
7.809
7.741
7.737
7.723
7.720
7.703
7.695
7.689
7.686
7.667
7.652
7.584
7.579
7.565
7.548
7.544
7.433
7.430
7.396
7.283
7.262
7.239
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.00
1.01
3.02
2.03
1.02
1.28

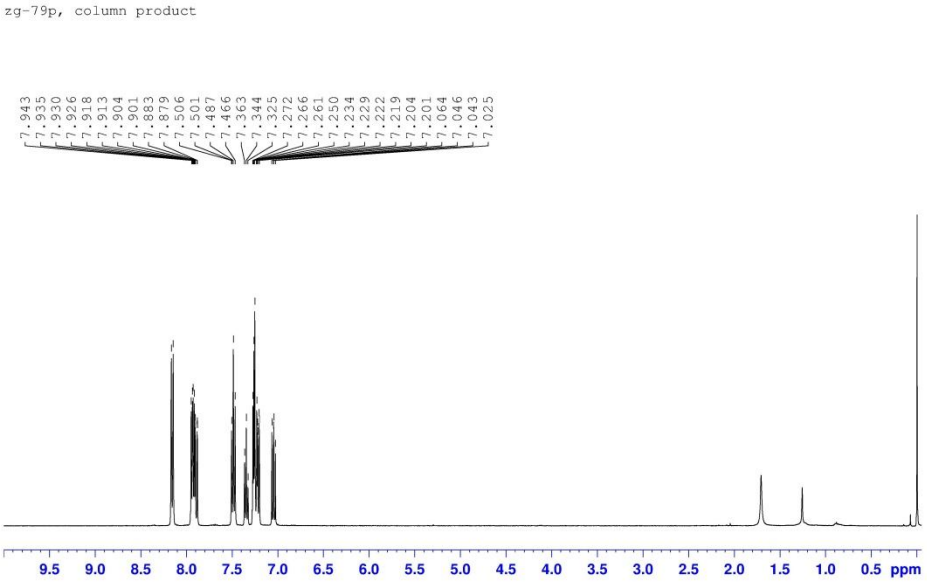

SZG 26
153.58
77.51
77.20
76.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

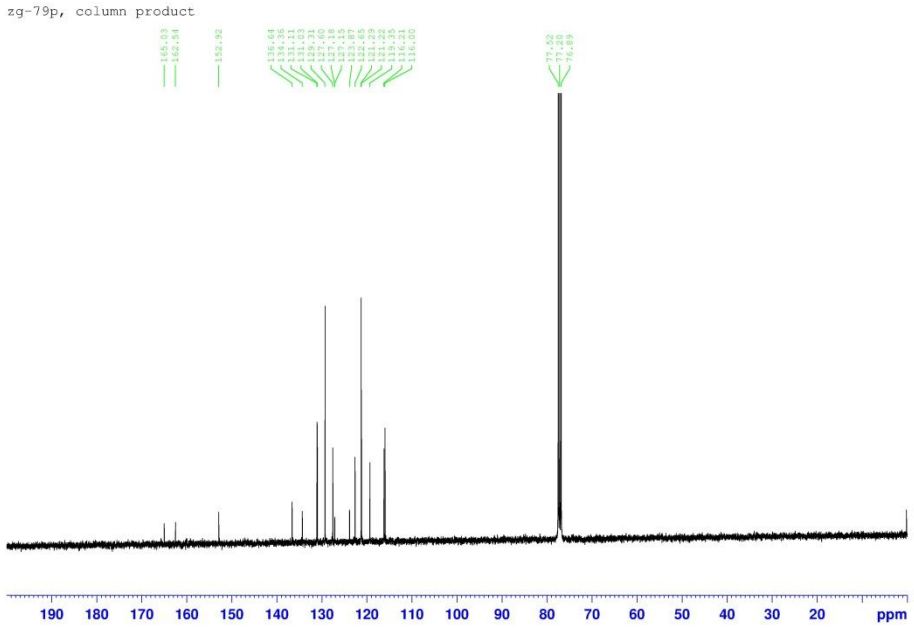
27. 
O
N
N
N
OMe

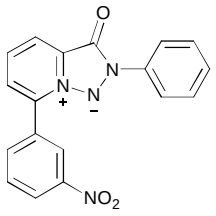

zg-71B, column product
8.196
8.193
8.174
7.914
7.909
7.892
7.863
7.860
7.841
7.838
7.504
7.485
7.464
7.355
7.337
7.318
7.213
7.210
7.195
7.192
7.082
7.060
7.052
7.034
7.031
7.013
3.906
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
2.02
1.01
2.06
1.04
1.05
3.09
3.12

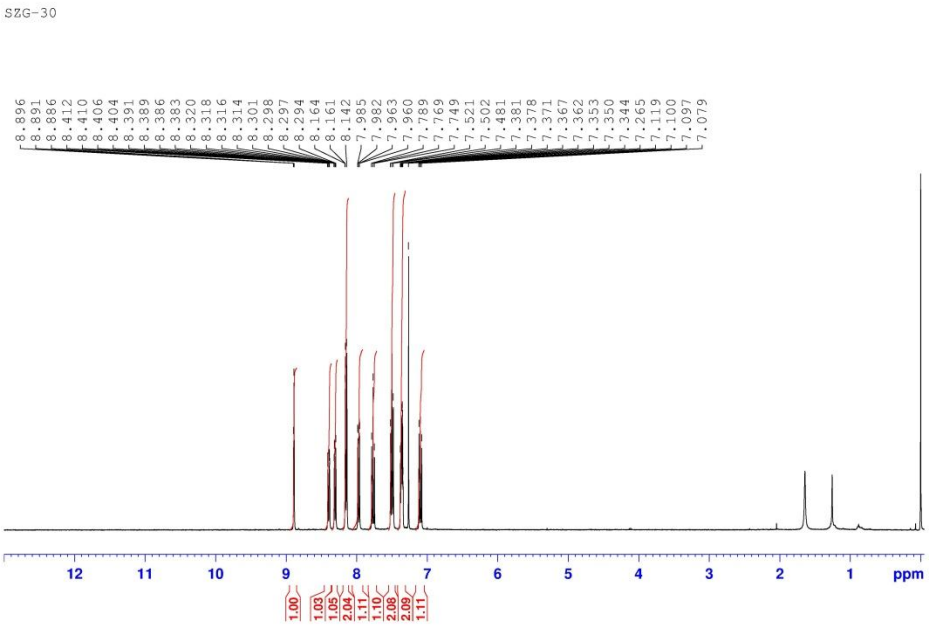

zg-71B, column product
161.20
152.96
136.79
135.27
130.44
129.27
127.87
125.60
123.38
121.98
121.33
120.83
119.46
114.32
77.52
77.20
76.89
55.63
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

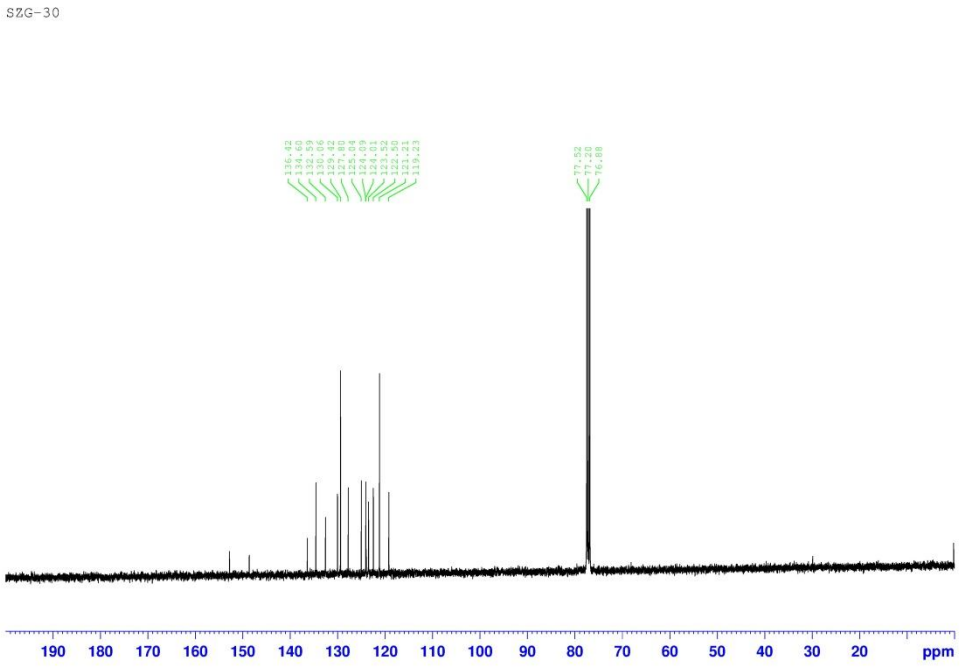
28. 

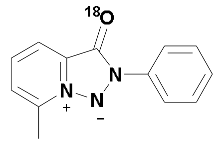

zg-79p, column product
7.943
7.935
7.930
7.926
7.918
7.913
7.904
7.901
7.883
7.879
7.506
7.501
7.487
7.466
7.363
7.344
7.325
7.272
7.266
7.261
7.250
7.234
7.229
7.222
7.219
7.204
7.201
7.064
7.046
7.043
7.025
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

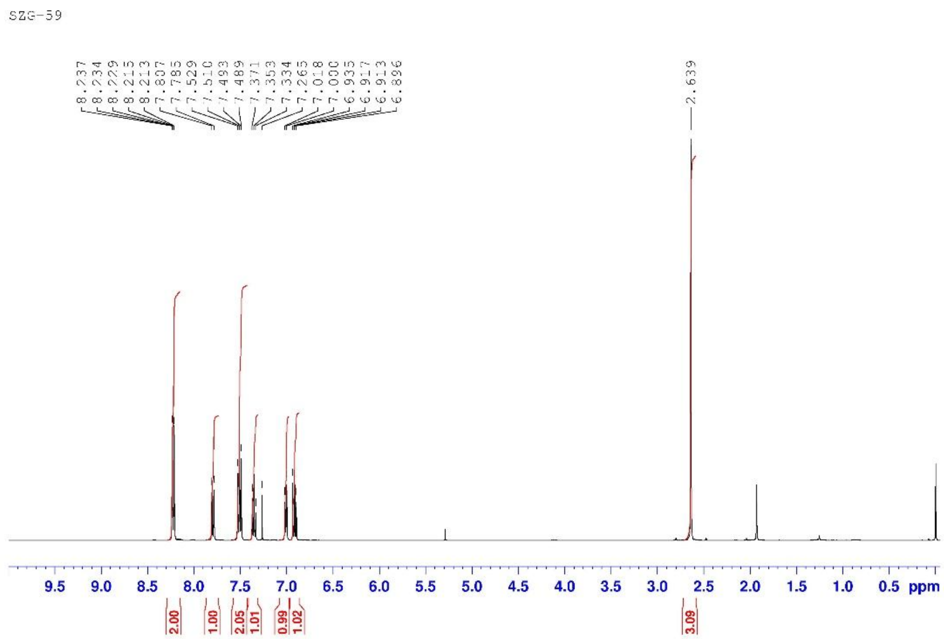

zg-79p, column product
165.03
162.54
152.92
136.64
134.16
134.11
131.03
129.31
127.60
127.18
127.15
123.87
123.80
121.29
121.22
121.15
116.21
116.00
77.52
77.20
76.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

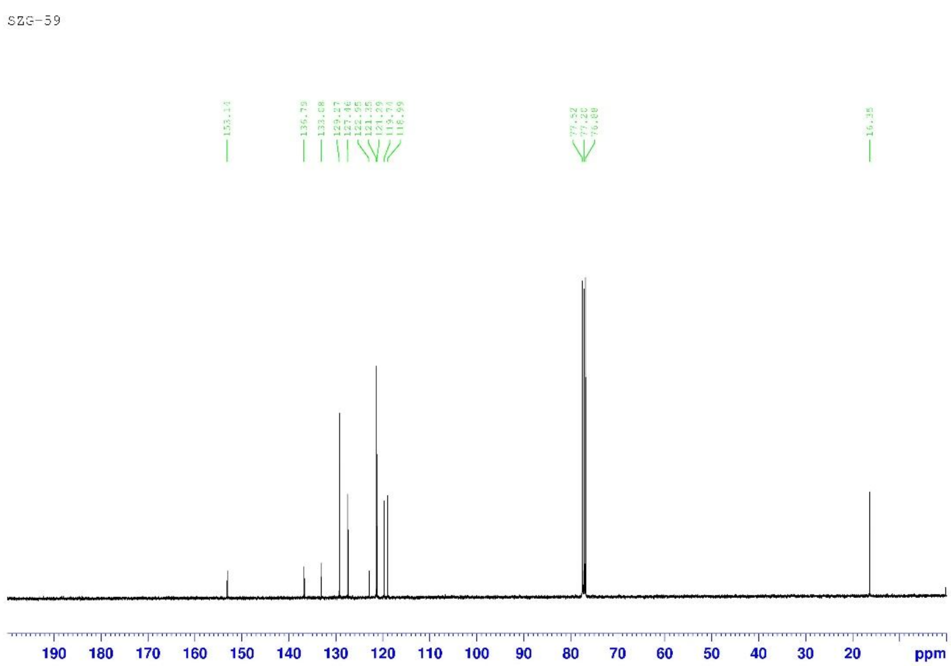
29. 

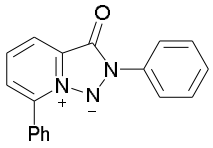

SZG-30
8.896
8.891
8.886
8.412
8.410
8.406
8.404
8.391
8.389
8.386
8.383
8.320
8.318
8.316
8.314
8.301
8.298
8.297
8.294
8.164
8.161
8.142
7.985
7.982
7.963
7.960
7.789
7.769
7.749
7.521
7.502
7.481
7.381
7.378
7.371
7.367
7.362
7.353
7.350
7.344
7.265
7.119
7.100
7.097
7.079
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.05
2.04
1.11
1.10
2.08
2.09
1.11

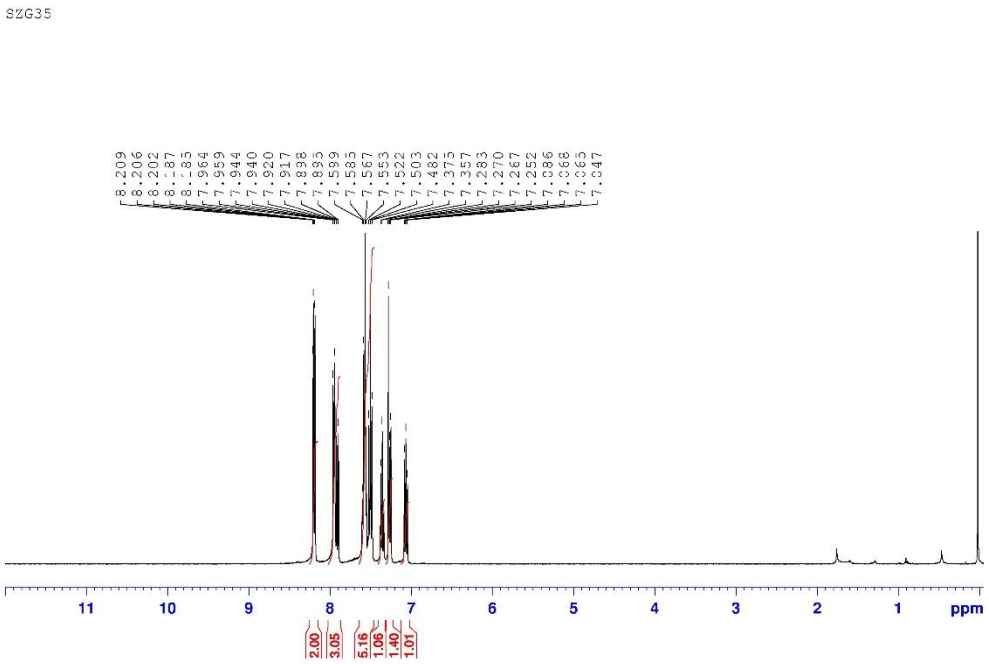

SZG-30
136.42
134.60
132.59
130.46
130.32
127.80
125.84
124.09
124.01
123.52
122.90
121.21
119.23
77.52
77.20
76.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

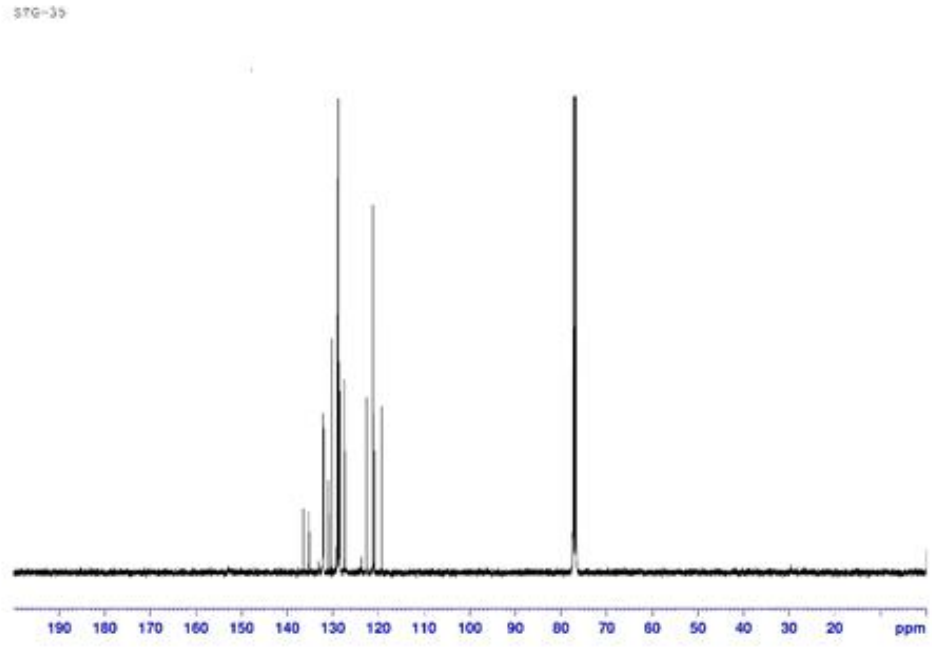
30. 


SZG-59
8.237
8.234
8.229
8.215
8.213
7.807
7.785
7.529
7.510
7.493
7.489
7.371
7.353
7.334
7.265
7.018
7.000
6.935
6.917
6.913
6.896
2.639
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
2.00
1.00
2.05
1.01
0.99
1.02
3.09

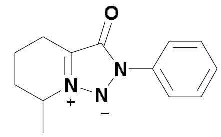

SZG-59
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

31. 
O
N
N
N
+
−
Ph

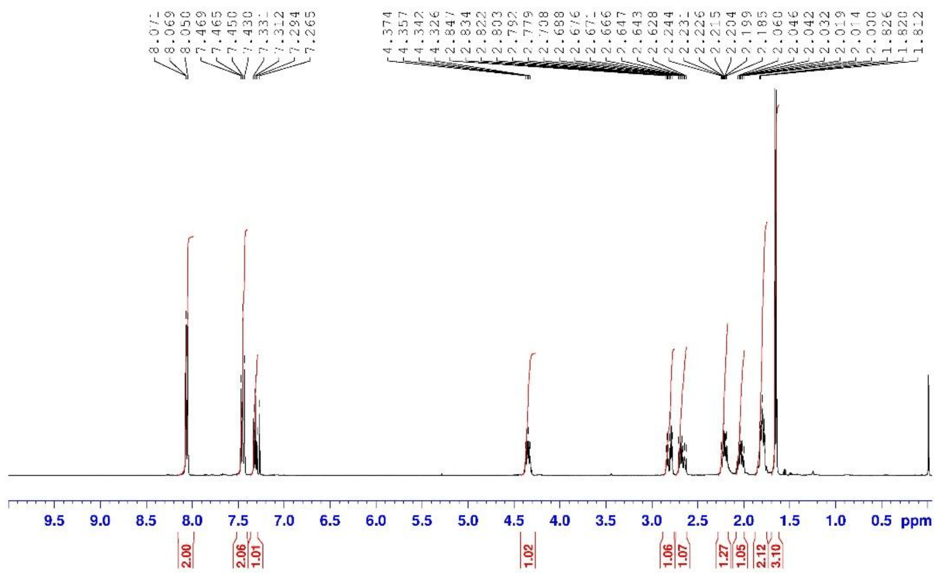

SZG35
8.209
8.206
8.202
7.964
7.959
7.944
7.940
7.920
7.917
7.898
7.893
7.599
7.583
7.567
7.553
7.522
7.503
7.482
7.375
7.357
7.283
7.270
7.267
7.252
7.086
7.068
7.065
7.047
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
3.05
5.16
1.06
1.40
1.01


STG-35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

32.



SZG 42



SZG-42